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Davita McTush-Camp

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I. KINETIC AND COMPUTATIONAL MODELING STUDIES OF DIMETHYLDIOXIRANE
EPOXIDATIONS II. ADDRESSING MISCONCEPTIONS ABOUT ENERGY CHANGES IN
CHEMICAL REACTIONS THROUGH HANDS-ON ACTIVITIES

by

DAVITA MCTUSH-CAMP

Under the Direction of Alfons Baumstark PhD

ABSTRACT

Kinetic studies determining the second order rate constants for the monoepoxidation of cyclic dienes, 1,3-cyclohexadiene and 1,3-cyclooctadiene, and the epoxidation of *cis-/trans*-2-hexenes by dimethyldioxirane (DMDO) were carried out using UV methodology. Consistent with published results, the kinetics of *cis-/trans*-2-hexenes by DMDO showed greater reactivity of the *cis*-isomer compared to that of the *trans*-compound. Molecular modeling studies for the epoxidation of a series of *cis-/trans*-alkenes, by DMDO were carried out using the DFT approach. The mechanism of epoxidation by DMDO was modeled by determining the transition state geometry and calculating the electronic activation energies and relative reactivities. The calculations were consistent with a concerted, electrophilic, exothermic process with a spiro-transition state for all cases. Kinetic studies for the monoepoxidation of the cyclic dienes showed a greater reactivity for 1,3-cyclohexadiene compared to that for 1,3-cyclooctadiene. The DFT

method was employed to successfully model the transition state for the monoepoxidation of the cyclic dienes by DMDO and successfully predict the relative reactivities.

Student misconceptions, at the high school and/or middle school level involving energy changes and chemical reactions have been prevalently noted in literature (by ACS and AAAS). Two examples of these misconceptions are: 1) heat is always needed to initiate a chemical reaction and 2) all chemical reactions create or destroy energy. In order to address these types of misconceptions, an educational module detailing the influence of energy changes on chemical reactions has been developed in conjunction with the Bio-bus program for middle and high school students. Visual aids and hands-on activities were developed in the module to potentially help students overcome/deal with the common misconceptions. Surveys were designed to assess the situations (determine the extent of the misconceptions) and the effectiveness of the educational module, before and immediately after the module and one-month later to determine retention. The educational module has been presented to approximately 100 high school students from underrepresented communities. Pre-survey data confirmed the presence of the common misconceptions reported in the literature. Data from the post-survey indicated the new instructional module enhanced the student's interest of science and expanded their content knowledge and laboratory skills. The post-survey data (immediately following the module) showed a significant difference in two out of five misconceptions when compared to the pre-survey data. However, this significance decreased when the 1-month post-survey data were compared to the pre-survey data.

INDEX WORDS: Dimethyldioxirane, Epoxidation, DFT, Kinetics, Computational modeling,

Chemical education research, Middle and high school science, Hands-on learning
manipulatives, Collaborative/cooperative learning, High school chemistry

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DAVITA MCTUSH-CAMP

A Dissertation Submitted in Partial Fulfillment of the Requirements for the Degree of

Doctor of Philosophy

in the College of Arts and Sciences

Georgia State University

2015

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Davita Patrice McTush-Camp
2015

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Georgia State University

May 2015

DEDICATION

My mother and father Vickie Elijah McTush and William Lennard McTush.

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I would first like to pay homage to the Lord God Almighty who has given me the skills and ambition to complete this doctoral degree and for having favor upon my life. I would like to thank my advisor Dr. A.L. Baumstark for the guidance of this research and for the endless support and encouragement that you have given me over the years. Thank you for believing in me and being there for me step-by-step along this entire process. I would like to thank Dr. Suazette Mooring for allowing me to work on your research project and for the willingness to help me experience my desires as a chemist. I would like to thank Dr. Vasquez for your assistance throughout this process. I would like to thank Dr. Germann for the support and research advice. I also would like to thank Dr. Barbara Baumstark and the Biobus for the love and support and for graciously welcoming me into the program so that I can embark on sharpening my teaching ability and assist in chemical education. Also thanks to the Mooring group members for the many talks and support given. I would also like to acknowledge the U.S. Department of Education for supplying me with the GAANN fellowship which funded the last three years of my doctoral study.

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thank you for your patience and supportive words when you knew mommy was hard at work. I started this journey when you were eight months and you have definitely been the person who has kept me going, I love you. To my sister Lucilia McTush, I cannot begin to express my gratitude to you. You have always been so supportive (the co-captain of my cheerleading squad) and always told me I would do great things, I thank God for blessing me with a caring, selfless, and thoughtful sister, I love you Sitter! To my mom and dad Jerome and Billie Camp, I want to thank you for endless love and support, it doesn't seem like our relationship is through marriage because of the love you two have shown and I thank you for that. I would also like to thank other family and friends Grandma Julia Mae, Carolyn, Grandma North, aunts, uncles, brother-in-laws, nieces, nephews, best friends/friends, line sisters, and a host of cousins. I appreciate all of your love and support.

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LIST OF ABBREVIATIONS

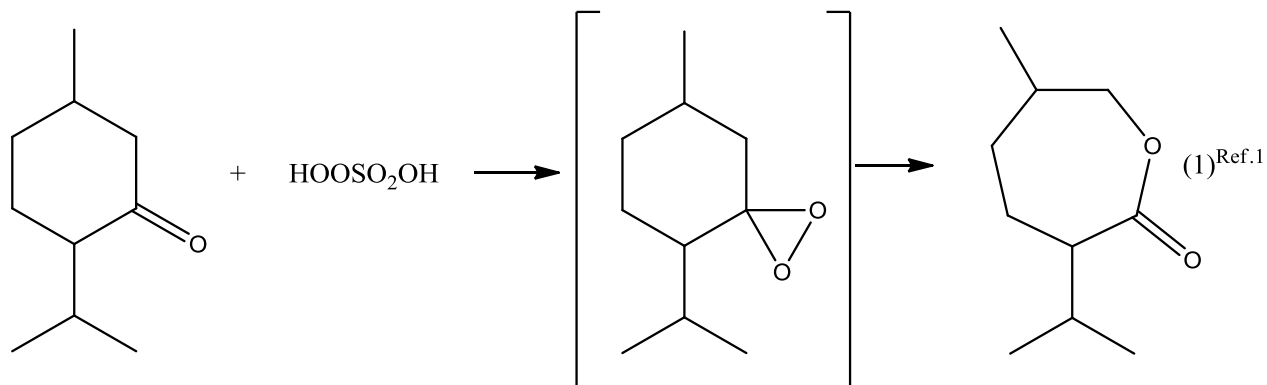
DMDO	Dimethyldioxirane
NMR	Nuclear magnetic resonance
GC-MS	Gas chromatography mass spectrometry
UV	Ultra violet
HPLC	High performance liquid chromatography
LFER	Hammett linear free energy relationship
HOMO	Highest occupied molecular orbital
LUMO	Lowest unoccupied molecular orbital
DFT-B3LYP	Density functional theory method hybrid Becke-Lee, -Yang
AM1	Austin model
IRC	Intrinsic reaction coordinate
ZPE	Zero point energy
TS	Transition state
Me	Methyl
Et	Ethyl
n-Pro	Propyl
i-Pro	Isopropyl
t-Butyl	Tert-butyl
STEM	Science technology engineering mathematics

CHAPTER 1: KINETIC AND COMPUTATIONAL MODELING OF DIMETHYLDIOXIRANE EPOXIDATIONS

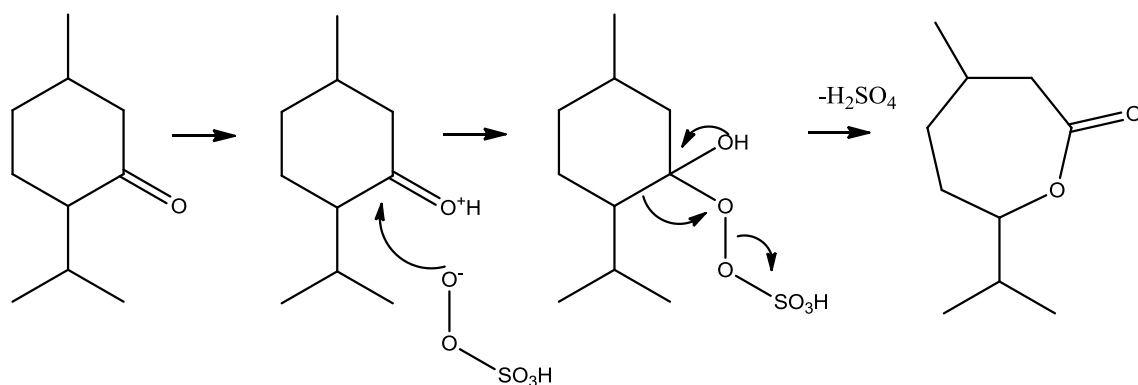
1.1 Introduction

1.1.1 Discovery of dioxiranes

Dioxiranes are members of the smallest cyclic peroxide group. Historically, the first three-membered cyclic peroxide structure was postulated by Baeyer and Villiger in 1899 as an intermediate in the Caroate oxidation of menthone.¹ Initially, a dioxirane was proposed as the key intermediate of the cyclic ketone (menthone) and monoperoxysulfuric acid reaction which afforded the corresponding lactone as shown in reaction 1 which was later shown to be incorrect.

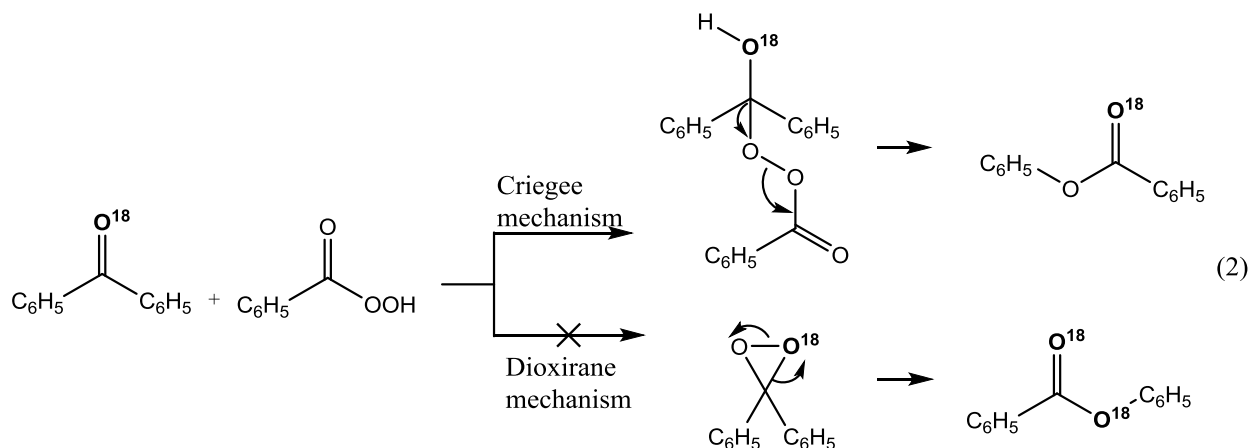


The current accepted Criegee-type mechanism proposed by Doering and Dorfmann forms the lactone through a peroxyketal intermediate (Scheme 1) rather than a dioxirane intermediate.²



Scheme 1 Accepted Criegee-type mechanism for the formation of lactone via a peroxyketal intermediate.^{Ref.2}

Doering and Dorfmann carried out this investigation by the reaction of ^{18}O -labeled benzophenone with perbenzoic acid. If the mechanism involved a dioxirane intermediate, both oxygen atoms of the phenylbenzoate would have been ^{18}O -labeled as shown in reaction 2 below. The analytical results showed that the carbonyl oxygen had the only one ^{18}O labeled atom in the final product. This established the Criegee-type mechanism as the likely process for the Baeyer-Villiger reaction.



The first verified report of a dioxirane synthesis appeared in 1972. Talbot and Thompson reported the synthesis of perfluorodioxirane in a patent.³ The synthesis consisted of F_2 oxidation of dilithioalkoxides to afford the perfluorodioxirane. However, because of the special reagent (F_2) this process is extremely limited and has not been expanded.

Montgomery discovered the in-situ generation of dioxirane in 1974. The initial discovery was based on kinetic studies of the catalysis observed in the decomposition of peroxymonosulfate.⁴ Addition of small amounts of ketones (acetone, 2-butanone, 3-pentanone, and cyclohexanone) were noted to decompose large amounts of Caroate, which indicated that the ketones behaved as catalysts to generate an intermediate (dioxirane).

In 1978, Sueram and Lovas accomplished the synthesis of the dioxirane parent system (Figure 1) by gas-phase ozonolysis of ethylene at low temperatures (-130 to -80°C).⁵ The structure of the parent dioxirane (Figure 1) was determined utilizing microwave studies.

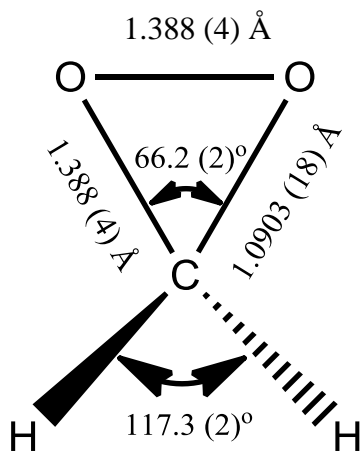
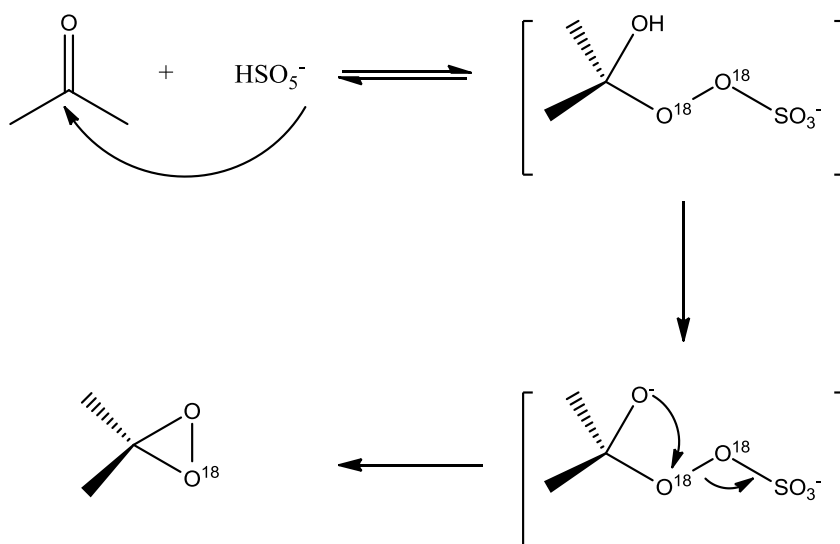


Figure 1. Structure of dioxirane calculated from the rotational transitions observed by microwave spectroscopy.

1.1.2 Generation of dimethyldioxirane

In 1979, Curci, Edwards et al. studied the decomposition of the biphasic mixtures of Caroate and acetone with 18-crown-6-ether acting as a phase transfer catalyst for the *in situ* generation of dimethyldioxirane.⁶ Curci, Edward et al. utilized ^{18}O -labeled Caroate and postulated that the labeled Caroate attacks the carbonyl group of the ketone following an intramolecular displacement to produce ^{18}O -labeled dimethyldioxirane as shown in Scheme 2.

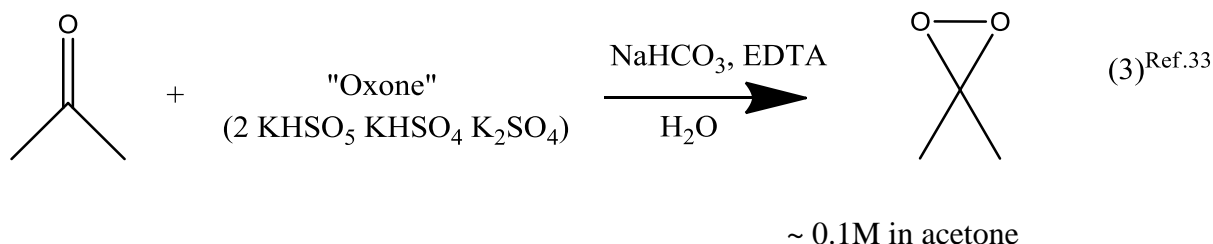


Scheme 2 Mechanism of dimethyldioxirane preparation for oxone.^{Ref.6}

1.1.3 Isolation of dimethyldioxirane

In 1985, Murray and Jeyaraman reported the first method of producing isolated dimethyldioxirane/acetone solutions via vacuum distillation.⁷ This achievement in dioxirane chemistry attracted the attention of the organic community because of the potential synthetic applications. An efficient method to prepare dioxirane is by the reaction of Caroate (which is commercially available as a triple salt of potassium peroxymonosulfate) and the appropriate

ketone. Dimethyldioxirane solutions could be conveniently prepared by the reaction mixture of Caroate, NaHCO_3 , distilled water, HPLC-grade acetone and EDTA to afford a pale yellow solution of dimethyldioxirane in acetone (reaction 3).



Isolated dioxirane solutions could then be used to carry out a variety of oxidations. The ^1H NMR spectrum of dimethyldioxirane has a singlet at 1.65 ppm and the ^{13}C NMR spectrum showing peaks around 22.7 ppm for the methyl groups and 102.3 ppm for the ring carbons.⁷ Adam et al. reported electronic (*ab initio* MP2 level of theory) calculations which predicted peaks for the ^{13}C NMR spectrum at 17.0 ppm for the methyl groups and 99.2 ppm for the ring carbons which were in good agreement with the experimental data.⁸

1.1.4 Dimethyldioxirane synthetic applications

Due to its ease of preparation from commercially available reagents, dimethyldioxirane has been used as a versatile oxidizing reagent during the past 35 years. Dimethyldioxirane is efficient in transferring oxygen to a variety of different systems, with high selectivity, under mild conditions. An advantage of using isolated dimethyldioxirane as an oxidizing agent is the ease of workup. The use of pure isolated dimethyldioxirane in acetone generally yields pure oxidized products in acetone. The dioxirane undergoes conversion to the solvent (acetone) during the course of the reaction. The solvent (acetone) and any remaining dioxirane are easily removed

under reduced pressure. The oxidized product often is analytically pure without the need of additional work.

The utility (reactivity and selectivity) of dimethyldioxirane oxidations has been extensively investigated.⁹ Oxidations performed by dimethyldioxirane have been found to be generally electrophilic in character and show retention of configuration. The most studied synthetic applications by dimethyldioxirane are epoxidation, heteroatom oxidation, and C-H (sigma bond) insertions. Dimethyldioxirane oxidations generally follow a S_N2 pathway and essentially have the following reactivity pattern: heteroatom oxidation > alkene epoxidation > secondary alcohol oxidation > CH insertion.

Epoxidation by dimethyldioxirane

Epoxidation is the most studied reaction in dioxirane chemistry.⁹ Isolated as well as *in situ* dimethyldioxirane methods can be used to epoxidize many different alkene systems including electron-rich, electron-poor, and unfunctionalized, as well as miscellaneous arenes and alkynes as shown in Figure 2. The preferred method of epoxidation of electron-rich alkene substrates is by use of isolated dimethyldioxirane.^{6a} For example, the synthesis of a hydrolytically sensitive compound, 8,9 epoxide *aflatoxin B*₁ (a well-known potent carcinogen) had failed using conventional epoxidation approaches but was successfully generated by the use of dry, isolated dimethyldioxirane solutions (transformation 1 in Figure 2).¹⁰

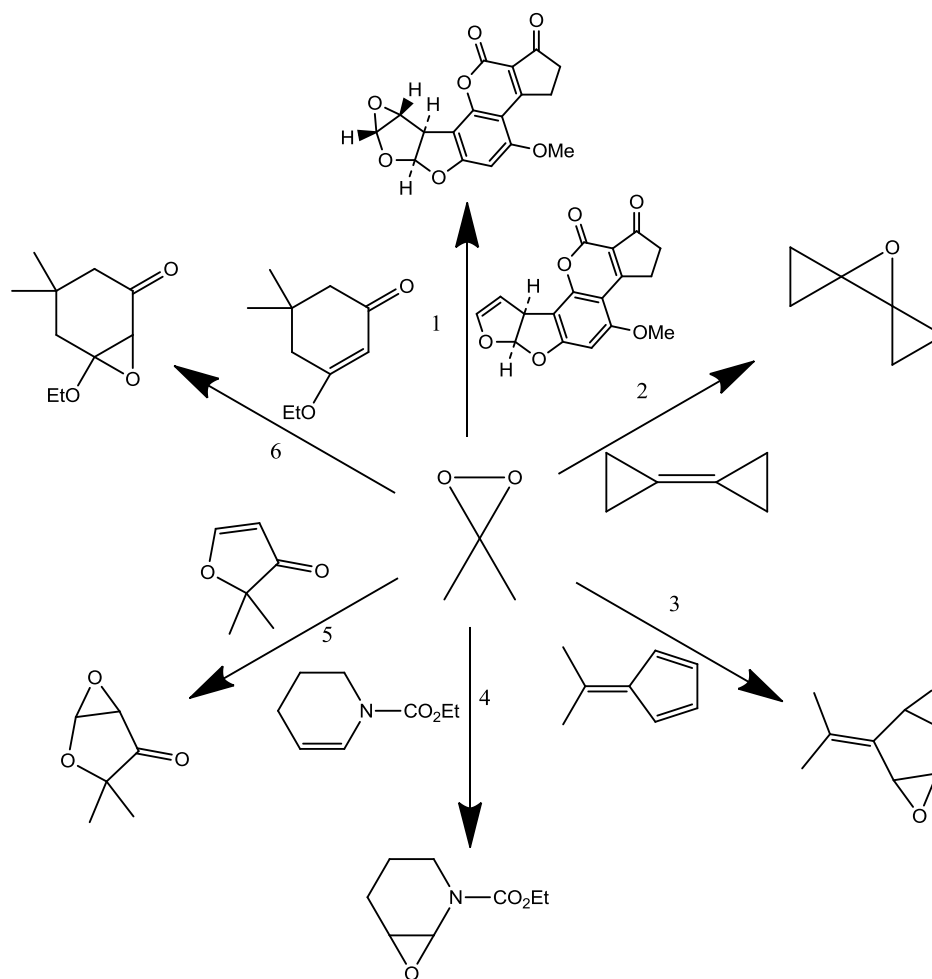


Figure 2. Selected epoxidations by DMDO.

Epoxidation of unfunctionalized alkenes by DMDO has been shown to proceed with excellent yields. The reaction of electron-poor alkenes with dimethyldioxirane was found to be the most difficult (transformation 4 in Figure 2) because of their inherent lack of reactivity. These deactivated compounds usually require the use of excess dimethyldioxirane, extended reaction times, and slightly higher reaction temperatures.¹² Alkenes with both electron donating and accepting substituents show similar reactivity trends with dimethyldioxirane as do electron-poor alkenes and therefore also require long reaction times, an excess of dimethyldioxirane, and

higher reaction temperatures (transformations 5 and 6 in Figure 2).¹² Heteroarene epoxidation by dimethyldioxirane have been shown to yield labile products therefore subambient temperatures must be used.¹³ Alkyne epoxidation by dimethyldioxirane leads to a mixture of products making it of extremely limited utility.¹⁴ Dimethyldioxirane epoxidation of chiral alkenes lead to diastereomeric epoxides with the diastereoselectivity depending both on the structure of the substrate and dioxirane.¹⁵

Heteroatom Oxidation by Dimethyldioxirane

Heteroatom functionalities are among the most reactive substrates towards electrophilic oxidation by dimethyldioxirane. Heteroatoms containing substrates with a nitrogen, sulfur, or phosphorus have been extensively studied dioxirane oxidations (Figure 3). The reactivity trends of heteroatom oxidation by dimethyldioxirane are $P > S > O$. The reactivity of nitrogen-containing substrates has been found to depend on the degree of alkylation and the hybridization state of the nitrogen.^{9a} Primary amines oxidation, as expected, can generate a mixture of products including hydroxylamine, nitro, nitroso, oxime, and azoxy compounds.¹⁶ A synthetically useful method for nitrogen oxidation uses excess dimethyldioxirane to oxidize aromatic and aliphatic amines to nitro compounds as shown in Figure 3 (transformations 1 and 2), respectively.¹⁷ Dimethyldioxirane oxidation of secondary amines with no α -hydrogens produces hydroxylamines which with excess dioxirane yields nitroxyl radicals.¹⁸

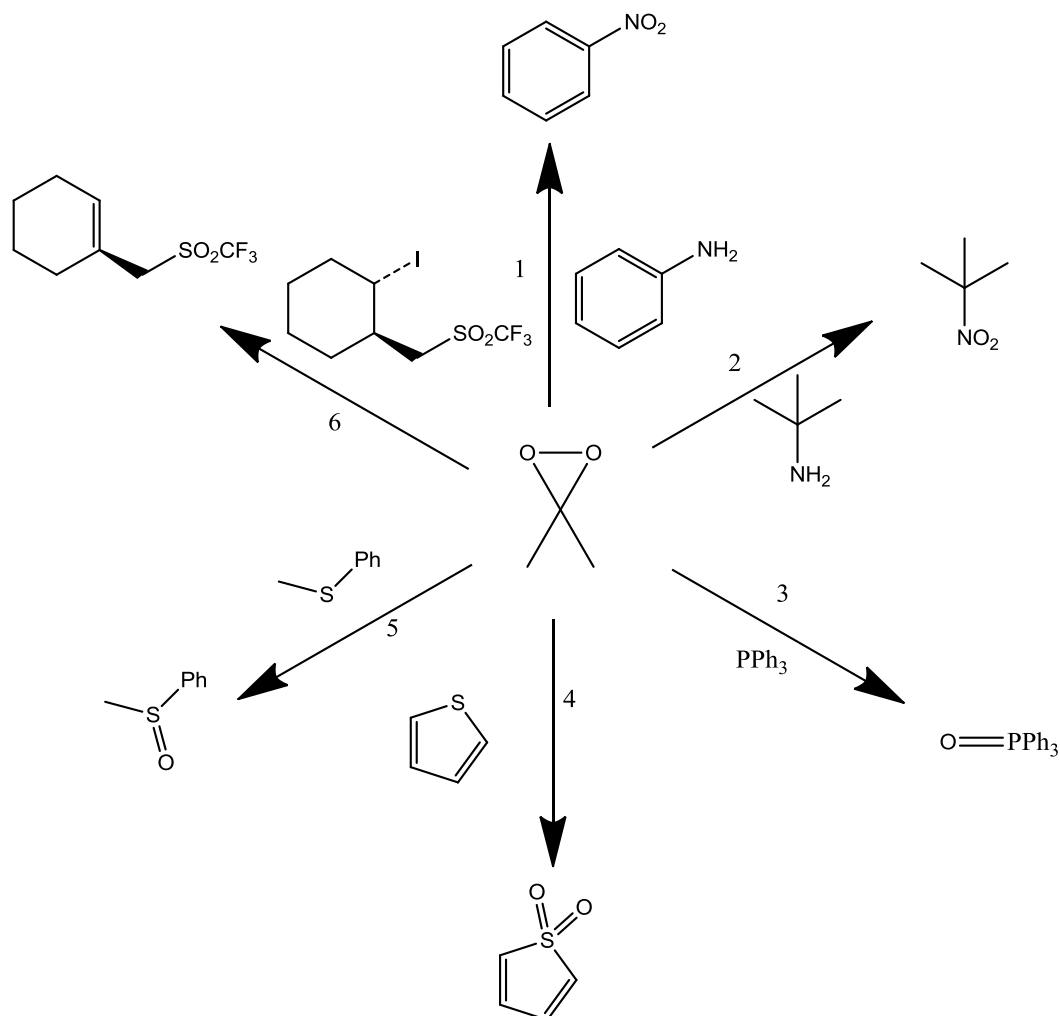


Figure 3. Heteroatom oxidation by DMDO.

Tertiary amine oxidation by dimethyldioxirane produces *N*-oxides, exclusively.¹⁹ Double bonded nitrogen-atom compounds such as an imino, oxime group are predominantly cleaved by dimethyldioxirane to produce the corresponding carbonyl compounds.²⁰ Oxidation of thiols by dimethyldioxirane affords a mixture of compounds including sulfonic acids, sulfinic acids, disulfides, thiosulfonates, and aldehydes which limits its synthetic utility.²² Conversely, generation of sulfones and sulfoxides from the oxidation of sulfides by dimethyldioxirane is of synthetic value (transformations 4 and 5 in Figure 3, respectively).^{9,23} Because of their high nucleophilicity, most trivalent phosphorus compounds are more reactive towards

dimethyldioxirane oxidation than the nitrogen-containing compounds (transformation 3 in Figure 3).^{7,21} As a result of this high reactivity, little is known about the selectivity of dimethyldioxirane oxidation of the phosphorus-containing compounds.²¹ Literature on dimethyldioxirane oxidations of other heteroatoms is very limited. However, there has been some research on the dimethyldioxirane oxidation of halogen-containing compounds. One of the first halogen oxidations by dimethyldioxirane leads to the production of hypochlorite anion from chloride ion.⁴ Iodine dimethyldioxirane oxidation is somewhat more prevalent in literature.^{7,24} Iodobenzene is oxidized by dimethyldioxirane to afford a mixture of iodylbenzene and iodosobenzene compounds.²⁵ Alkyl iodides are converted to their unstable oxidation intermediate which eliminates the oxidized iodine functionality to yield the corresponding alkene (transformation 6 in Figure 3).²⁶

CH insertions by dimethyldioxirane

CH insertion by dimethyldioxirane is found to be of limited usage in dioxirane chemistry due to the lack of reactivity of the dioxirane.⁹ These transformations (Figure 4) can occur under very mild conditions, at subambient temperatures with both *in-situ* and isolated dimethyldioxirane. Dimethyldioxirane is usually suitable for some of these conversions but because of the inherent long reaction times the more reactive trifluoromethyl dioxirane (TFD) is usually needed.²⁷ In general, CH-insertions have been extensively studied and show the following reactivity trend: primary < secondary < tertiary < benzylic < allylic C-H bonds.⁹ The initial alcohol products from primary and secondary alkane's initial alcohol products are generally further oxidized to carbonyl compounds since the α -hydrogen next to the alcohol functionality tends to be more reactive towards dioxirane oxidation vs. the starting alkane

(transformations 1 and 2 respectively in Figure 4).^{27,28} This over-oxidation is even more prevalent in the oxidation of benzylic compounds (transformation 3 in Figure 4).²⁹

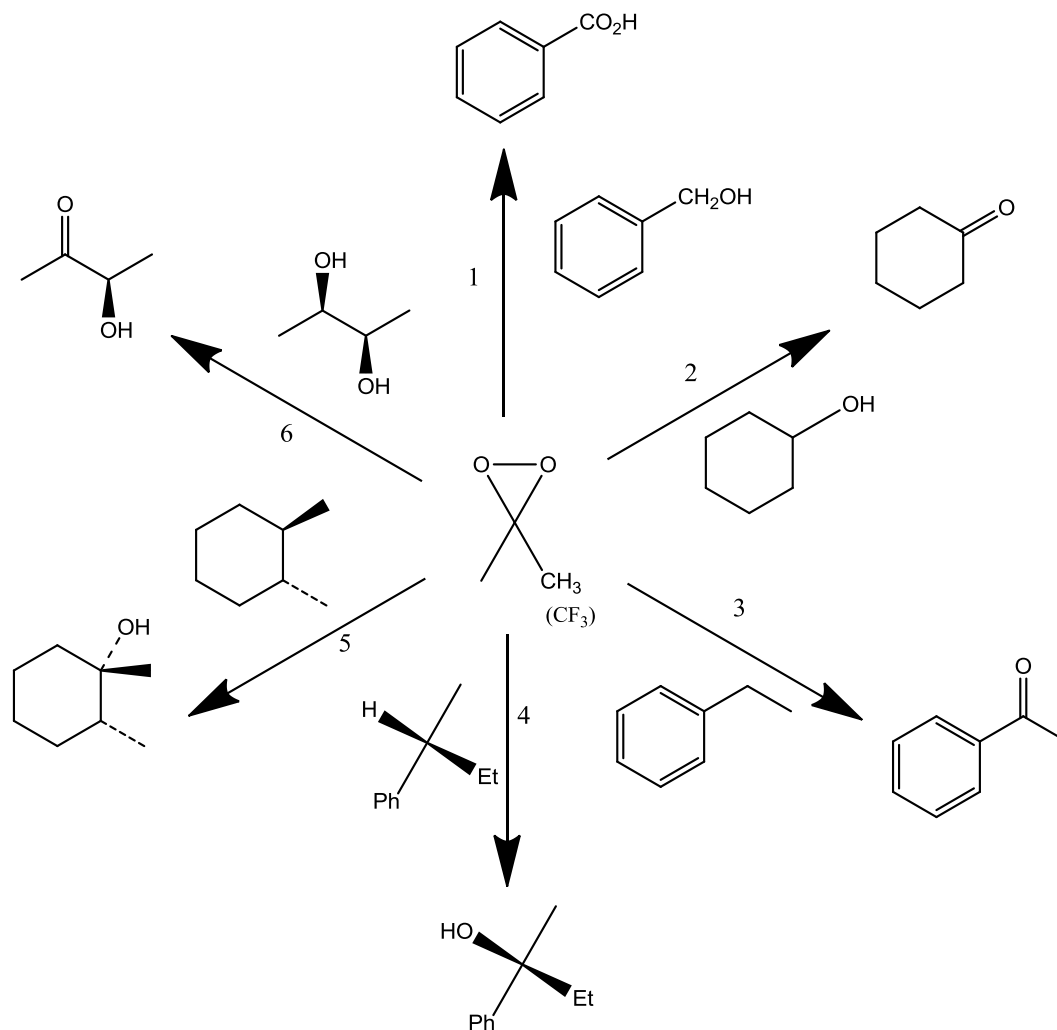


Figure 4. C-H insertion by DMDO.

The over-oxidation has not been observed with tertiary alkanes therefore tertiary alcohols are produced (transformations 4 and 5 in Figure 4) in high yields.^{17a} It is important to mention that C-H bonds adjacent to aldehydes, carboxylic acids, ketones, sulfonates, sulfones, sulfonic acids, nitriles, and amides tends to be unreactive towards dimethyldioxirane C-H insertion, even for the more reactive dioxirane TFD.³⁰ The reported results have shown that C-H insertions are very stereoselective.^{17a,31} For example, retention of configuration was observed for oxidation of

cis- and *trans*-dimethylcyclohexanes and *trans*-decalin.^{17a} The reactivity of the C-H bond that is adjacent to a functional group depends on the nature of the functional group.^{9,32} As already mentioned above some functional groups appear to reduce the reactivity of the adjacent C-H bonds. For an example, the C-H bond adjacent to a nitro functionality is unresponsive to dimethyldioxirane oxidation.

1.1.5 Dimethyldioxirane epoxidation of simple alkenes: Reactivity trends and mechanism

As previously mentioned, epoxidation by dimethyldioxirane has been extensively studied. There have been studies that have reported reactivity trends as well as selectivity. Utilizing dimethyldioxirane as an oxidizing agent for alkenes provides many benefits which include the ease of preparation, mild conditions, selectivity, and the flexibility of reaction conditions. In addition the use of isolated dimethyldioxirane often yields the pure epoxides (oxidized product) since the dimethyldioxirane is converted to the solvent during the reaction which can be readily removed in most cases.

Reactivity trends

As previously noted, dimethyldioxirane epoxidation has been found to be stereospecific with complete retention of configuration with respect to the original substrate. Epoxidation of *cis*-alkenes produced the corresponding *cis*-epoxides while epoxidation of *trans*-alkenes produced the corresponding *trans*-epoxides. Kinetic studies by Baumstark et al. examined reactivity trends of dimethyldioxirane epoxidation.^{11b, 33} The epoxidation was shown to be first order in dimethyldioxirane and in the alkene substrate (second order overall). Studies revealed that tetrasubstituted alkenes were two orders of magnitude more reactive than monosubstituted or *trans*-dialkyl compounds.^{11b} Kinetic studies also revealed that *cis*-alkenes were more reactive than their *trans*-isomers, with the exception of phenyl substituted alkenes.^{11b,33} The reactivity

ratio ($k_{2\text{cis}}/k_{2\text{trans}}$) could be up to 20 fold difference depending on the size of the substituents (larger alkyl groups displayed a higher reactivity difference) and thus of synthetic interest and utility. The relative reactivity series for dimethyldioxirane epoxidation is qualitatively similar to other electrophilic oxygen-atom transfer reagents such as peracids. However, there are some surprisingly differences between dimethyldioxirane epoxidation and other electrophilic oxygen transfer agents, such as peracids, epoxidations. The relative reactivity series for epoxidations by peracids and α -azohydroperoxides increases as the number of substituents increases.^{34,35} While epoxidation by dimethyldioxirane is much less sensitive to the number of substituents and is dependent on the size of the substituent.^{11b,33} It was also noted that using wet acetone in preparing dimethyldioxirane stock solutions for kinetic studies increased the k_2 values significantly.^{33a} In order to achieve reproducible results dry solutions of dimethyldioxirane in acetone were required.

Mechanism

Based on a Hammett-type study on the S-oxidation of substituted thioanisoles by dimethyldioxirane, Murray et al. concluded that dioxirane is electrophilic in character, with a ρ value of -0.77.³⁶ Contrastingly, Adam et al., measuring the product ratios of the reaction of thianthrene-5-oxide with isolated dimethyldioxirane, initially concluded that dimethyldioxirane showed considerable nucleophilic character.⁸ However, the conclusions from this study were later ammended due to the discovery of errors and subsequent corrections. The ρ value of dimethyldioxirane epoxidation was slightly lower compared to those of other electrophilic oxygen-atom transfers (α -azo hydroperoxides, flavin 4a-hydroperoxides, and hydrogen peroxide all displaying ρ values of -1.2, -1.7, and -1.2, respectively) Murray's conclusion of the electrophilic character of dioxirane is consistent with the experimental epoxidation data.

Furthermore, the study of the effect of added water mole fractions (~ 0.15) to the epoxidation of a series of substituted styrenes resulted in a larger ρ value compared to the ρ value of the epoxidation in dried acetone.^{33a} The magnitude and sign of the ρ value correlated with expectations for electrophilic oxygen atom transfer.

The observed reactivity differences for epoxidations of *cis*-/*trans*-alkenes, which are of synthetic utility, have generated a great deal of interest in understanding the mechanism of dimethyldioxirane epoxidation. Two mechanistic extremes for the electrophilic oxygen transfer process were postulated: planar or spiro. Historically, Bartlett had suggested a cyclic planar concerted process (butterfly planar) for the epoxidation of alkenes by peracids.³⁴ This concept was generally thought to apply to all epoxidations regards of reagent. Davis has described the oxidation of alkenes by oxaziridines as planar (butterfly-type) after a detailed study with chiral oxaziridines.³⁸ The mechanism for the oxygen-transfer reagent dimethyldioxirane can also be viewed as either “butterfly-planar” (Figure 5) or spiro transition state (Figure 6). The observed relative reactivity result of epoxidations by dimethyldioxirane seems to correlate well with the spiro transition state and not the butterfly approach. The spiro transition state allows the oxygen-atom transfer to occur favorably with the *cis*-isomer since one side of the alkene can be attached preferably. This agrees with the greater reactivity of the *cis*-alkenes since there are less steric interactions between the *cis*-isomer and dimethyldioxirane in the spiro-transition state orientation compared to the *trans*-isomer and dimethyldioxirane.

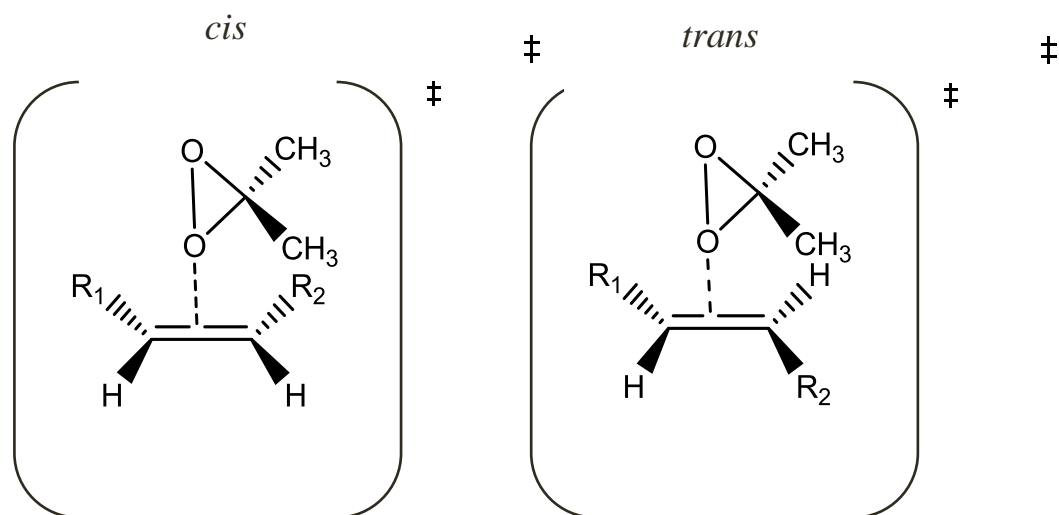


Figure 5. Butterfly-planar transition state orientation for the epoxidation of *cis*- and *trans*-alkenes by DMDO.

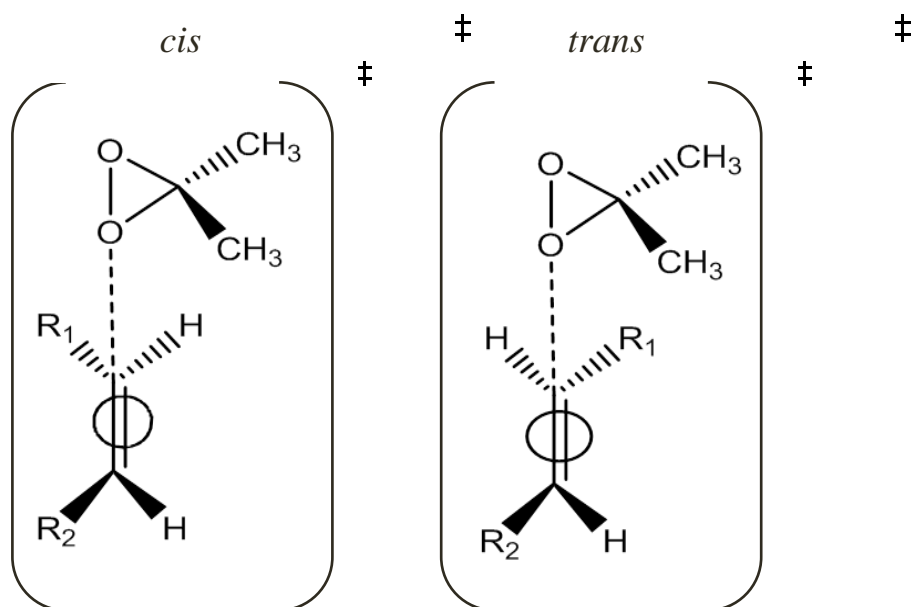


Figure 6. Spiro transition state orientation for the epoxidation of *cis*- and *trans*-alkenes by DMDO.

1.1.6 Theoretical/Computational modeling of dimethyldioxirane epoxidation

The advancement of computational chemistry provided a valuable approach to gain insights on the structural and mechanistic properties of dimethyldioxirane and epoxidation. Concerning the chemical reactivity of dioxiranes, Cremer et al. calculated the strain energy for the parent dioxirane to be 26 kcal mol⁻¹ comparable to that of cyclopropane whose strain energy is 26.5 kcal mol⁻¹.³⁹ Due to computational limitations at that time, dimethyldioxirane strain energy could not be determined. More recent calculations by Bach et al. concluded that the parent dioxirane is much less strained than expected, with a strain energy value of 18 kcal mol⁻¹ (using a larger basis set for the calculation).⁴⁰ That group also concluded that the calculated strain energy of dimethyldioxirane could be as little as 11 kcal mol⁻¹ which offset any preconceived notions that dioxiranes are highly reactive due to their high strain energy. The group concluded that the low strain energy was due to the germinal dimethyl and dioxa substitution along with the rather strong carbon-methyl bonds of the dioxirane.

Computational studies were also able to aid in resolving the argument of the electronic character of the oxygen transfer, whether dioxiranes are nucleophilic and/or electrophilic oxidizing agents. To answer this mechanistic question, Deubel et al. used advanced quantum-chemical methods to calculate transition state structures of epoxidation of alkenes substituted by electron withdrawing and donating groups, by the parent dioxirane and peroxy-formic acid.⁴¹ The authors determined that the electronic character depended on the substituents of the alkene. The data shows that peroxy-formic acid was an electrophilic oxidant regardless of the substituents of the carbon-carbon double bond. The parent dioxirane was predicted to be of electrophilic character for alkenes that have electron-donating groups (amino, methyl, and vinyl) and

nucleophilic for alkenes that have electron-withdrawing groups (cyano and carbaldehyde). They ultimately characterized the dioxirane as being biphilic in nature.

Numerous computational studies have been found on the transition state structure of dioxirane epoxidations.⁴²⁻⁴⁸ The transition state structure appears as if the pi bond of the alkene attacks the peroxide bond of the dioxirane resembling a S_N2 -type process. All of the computational investigations of epoxidation have concluded that the process was concerted and electrophilic with a spiro transition state in agreement with the conclusion made by Baumstark et al based on experimental error.^{11b} The preferred molecular geometry of the spiro transition state has the dioxirane substituents directed away from the alkene substituents, decreasing the effect of steric interactions in the resulting transition state. (Figure 7), which is not possible in the Bartlett butterfly planar orientation (Figure 8).

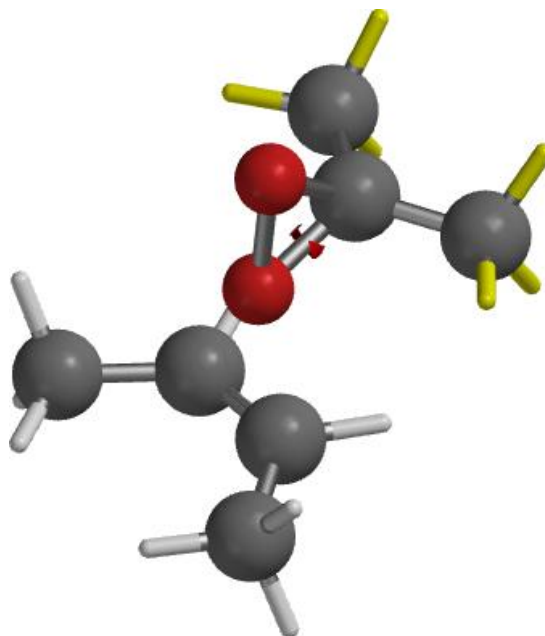


Figure 7. Spiro approach in the reaction of *cis*-2-butene with DMDO.

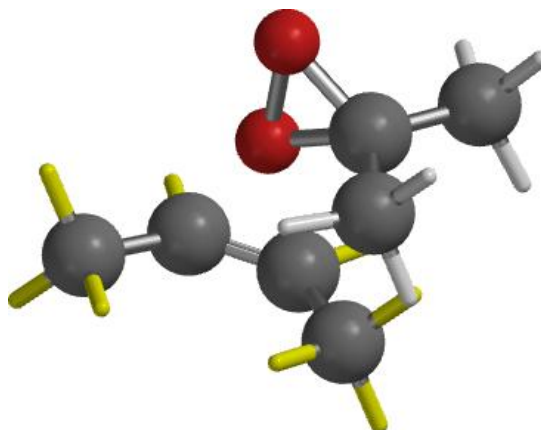


Figure 8. Planar approach in the reaction of *cis*-2-butene with DMDO.

Semiempirical (AM1) calculations were utilized to model dimethyldioxirane epoxidation of simple alkenes within a structurally homologous series.^{33b} This approach saved time but failed when comparisons between series were needed. Density Functional Theory (DFT) calculations were used to model the epoxidation of ethylene, propene, and *cis*- and *trans*-2-butene by the parent dioxirane as well as dimethyldioxirane, and predicted a spiro transition state in agreement with the mechanism postulated based on experimental data.⁴³⁻⁴⁴ Ab initio calculations, employed to model *cis* and *trans* epoxidations by dimethyldioxirane also predicted a spiro transition state and the correct relative reactivity of *cis* vs. *trans* simple alkenes.⁴⁶ Basic gas phase density functional theory calculations (DFT) proved to be effective for modeling the epoxidation of α,β -unsaturated esters by dimethyldioxirane as well as for the epoxidation of several acyclic conjugated dienes (*s-trans* systems) by dioxirane, systems for which steric effects are minimized.⁴⁷⁻⁴⁸ Calculations in the gas phase as well as in acetone were determined by Bach et al. for dimethyldioxirane epoxidations at the DFT B3LYP level basis set.⁴² Results showed that the reactivity of the epoxidation by dimethyldioxirane was comparable to that of peroxy-formic acid in the gas-phase. However, the energy of activation of dimethyldioxirane epoxidation in

acetone decreased drastically because of the polar stabilization provided by the solvent. Similarly, the integration of one water molecule in the transition state structure for the cyclohexene epoxidation by dimethyldioxirane lowered the energy of activation from 12.6 to 8.5 kcal mol⁻¹, and the inclusion of two water molecules lowered it to 6.3 kcal mol⁻¹, which is consistent with experimental data.

Statement of Research

An investigation of the kinetics of the epoxidation of a *cis*-/*trans*-alkene pair and the subsequent computational modeling of the epoxidation of two series of *cis*-/*trans*-alkene pairs by dimethyldioxirane was undertaken. This study provides insight into the electronic and structural influences that affect the epoxidation. The kinetic study of the epoxidation of a new *cis*-/*trans* pair of alkenes, *cis*-2-hexene and *trans*-2-hexene, by DMDO should provide data there are intermediate to the established steric factors that affect the rate of epoxidation of several *cis*-/*trans*-alkene pairs by DMDO. The computational modeling study of 2 series of *cis*-/*trans*-dialkyl substituted alkene pairs will contribute to the understanding of the important factors that affect the rate of epoxidation. The first series of alkenes to be modeled have a methyl substituent at one side of the double bond as a constant with the other substituent increasing in steric bulk (increased branching) along the series. The second series has a constant ethyl substituent at one side of the double bond as a constant while the other substituent having increasing in steric bulk (increased branching) along the series. Each series is designed to evaluate the effect of increasing steric bulk (the size of the substituent) on the rate of epoxidation. Using the DFT approach, the transition state orientations will be evaluated to determine if the varied substituents at the double bonds will affect the geometry of the oxygen insertion reaction. The relative reactivities will be

evaluated by determining the electronic relative reactivities and activation parameters for both *cis*-/*trans*-alkene series. The results will be compared to the experimental values.

1.2 Experimental

1.2.1 General information

All glassware for the preparation of dimethyldioxirane and kinetic studies was placed in a 1% Na₂EDTA boiling solution for 30 minutes, rinsed with deionized water and acetone, and allowed to dry in the oven. All solvents used were HPLC grade (Aldrich). *cis*-2-Hexene and *trans*-2-hexene were commercially available and purchased from Aldrich. Substrate (alkene) solutions were prepared using HPLC grade acetone (dried over Na₂SO₄) and used immediately. The kinetic experiments were run on Shimadzu UV-3101 PC spectrometer with jacketed cells equipped with a circulating water bath. The temperature of the kinetic experiment solutions were measured with a YSI calibrated thermometer probe (Yellow Spring Instrument Co. Inc., YSI, model 42SC (error $\pm 0.1^{\circ}\text{C}$)).

1.2.2 Preparation of dimethyldioxirane

Solutions of isolated dimethyldioxirane were prepared according to the method described in literature by Murray et al. with minor modifications developed by our research group.⁷ A three-neck round bottom flask was equipped with an equalizing addition funnel, solid addition funnel, and an air condenser packed with glass wool attached to a receiving flask that was placed in a Dewar cooled to -78°C in a dry/ice acetone mixture. A mixture of EDTA (1g, 0.0029 mole), sodium bicarbonate (72 g, 0.85 mole), water (60 mL), and acetone (45 mL) and a magnetic stir bar was added to the three-neck round bottom flask and allowed to stir at room temperature. Oxone® (150 g, 0.24 mole) was added in small portions over 20 minutes, and the pressure-

equalized dropping funnel containing a mixture of 60 mL of water and 40 mL of acetone (HPLC grade, Aldrich), was added drop-wise to the contents of the three-neck round bottom flask, simultaneously. After the addition of the oxone and acetone solution the pressure of the reaction system was gradually decreased to ~110 mmHg and the product collected in the cold trap. The mixture was stirred vigorously at room temperature until the reaction was complete (no more signs of CO₂ being released). After the reaction was complete, dimethyldioxirane/acetone azeotrope was removed from the receiving flask and concentrated via redistillation at 10°C and ~8 mmHg. Dimethyldioxirane/acetone solution was then dried over anhydrous sodium sulfate and stored at -22°C (stable weeks without appreciable decomposition). The concentration for the dimethyldioxirane/acetone mixture was determined by UV technology. The absorbance of dimethyldioxirane at 330 nm was measured and the concentration was calculated by using Beer's law with an ϵ (the molar absorptivity constant of dimethyldioxirane) of 12.9 L mol⁻¹ cm⁻¹.

1.2.3 Kinetic study of *cis*- and *trans*-2-hexene

Kinetic studies were carried out on a Shimadzu UV-3101 PC spectrometer with jacketed cells. All solutions used in the kinetic studies were prepared with HPLC-grade dried acetone. The disappearance of dimethyldioxirane was monitored vs. time at 330 nm for at least two half-lives. Pseudo-first order conditions were implemented for each kinetic experiment where an excess of either substrate or dimethyldioxirane was utilized in a 10:1 ratio. A solution of dimethyldioxirane in dried acetone (1.0 equiv. known concentration) was placed in the jacketed 1 cm UV quartz cuvette and was allowed to thermally equilibrate at 23°C. Soon after, the appropriate amount (10 equiv.) of alkene stock solution in dried acetone was added rapidly (via syringe) and mixed for ~5 s via pipette. Kinetic data were analyzed and corrected for to give a linear pseudo first order plot where the slope of the line is equal to the k observed (k_{obs}) (Figures

9 and 10). All kinetic runs had correlation coefficients of 0.99 or greater and the k_2 values are the average of at least 3 separate experiments. The calculation of the second order rate constants is as follows:

$$k_2 = k_{\text{obs}} / [\text{reagent in excess}]$$

$$k_{\text{obs}} = \text{slope of the line for the pseudo first order plot}$$

$$[\text{reagent in excess}] = \text{Concentration of the reagent in excess}$$

1.2.4 Computational modeling

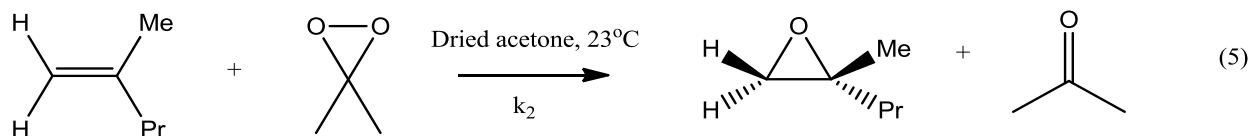
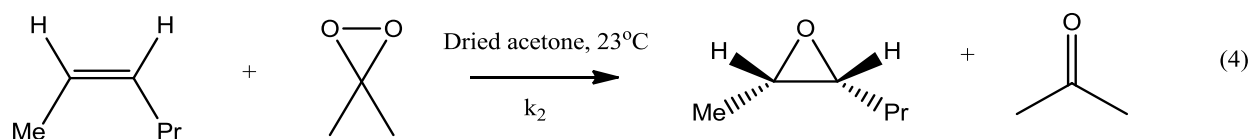
Computational modeling was carried out using the Density Functional Theory (DFT) approach using Becke3-LYP and the 6-31 G basis set (the gas phase). All calculations were performed with the Spartan'10 molecular modeling program. Energies for the minimized ground state structures were determined for all the reactants (dimethyldioxirane, *cis*-alkenes and *trans*-alkenes) and the products (acetone, corresponding epoxides). As expected, the computational data predicted that the reactions are exothermic for all cases. The optimized ground state energy structure of each alkene was checked by frequency calculations to ensure the global minima were reached. All approaches to the reaction sites were calculated. As expected, the optimized transition state resulted in a spiro-orientation, regardless of the initial approach of the dioxirane, for all cases. The lowest electronic activation energy transition state value was taken as representative. The calculations that were carried out with the methyl groups of the dioxirane oriented away from the most hindered side of the alkene (Figure 12) was taken to be the major contributor of the overall reactivity and always yielded the lowest energy spiro transition state. Each transition state calculation was checked for validity showing only one negative eigenvalue. This eigenvalue also corresponded to the eigenvector in a separate intrinsic reaction coordinate

(IRC) calculation. When animated, the IRC linked the starting materials to the desired products through the spiro-oriented transition state. To minimize conformational differences the conformations of the alkyl groups of the optimized alkenes were checked compared to those of the alkyl groups in the transition state. Comparisons that showed the basic orientations were equal in both the transition state and the alkene as well as having no significant added steric interactions with the dioxirane did not affect the value of the electronic activation energies. These instances showed that the calculated energies of the starting materials and the transition state both reflected the increased conformational effects but the electronic activation energies were unaffected. HOMO-LUMO energies were obtained from the optimized geometries using the Density Functional Theory (DFT) approach using Becke3-LYP and the 6-31 G basis set. The electronic activation energies were calculated as follows: $E_{\text{elect.}} = \text{Energy of transition state} - (\text{Ground state energy of dioxirane} + \text{Ground state energy of substrate})$. The relative reactivities were calculated by taking the difference in the electronic activation energies and applying the value to the Arrhenius equation in the following manner: $k_2\text{rel} = (e^{(-\Delta E_{\text{elect.}}/RT)})$ (k_2 normalized). The substrate with the lower reactivity is normalized to 1. Inclusion of a solvent in calculations while affecting the individual values, did not affect the electronic activation energy differences in agreement with the literature.⁴¹⁻⁴⁵ Therefore, all calculations were completed in the gas phase at 23°C. The entropies on the energies were not determined. A phantom atom (Z) was placed in the center of the C-C double bond of the alkene to measure the angles of the plane of the alkene and the peroxy oxygens of the dioxirane. Valerie Stone, an undergraduate student working in the Baumstark research group at the time helped with the molecular modeling calculations and contributed to the publication of this research topic.

1.3 Results

1.3.1 Epoxidations of *cis*- and *trans*-2-hexene

Kinetic studies for the determination of second order rate constants for a pair of *cis*-/*trans* pair of simple alkenes (*cis*- and *trans*-2-hexene) were carried out using UV technology at 23°C at 330 nm. For each kinetic study the disappearance of dimethyldioxirane (decrease in absorbance at 330 nm) was monitored vs. time. Pseudo first order conditions were employed to carry out the kinetics. The concentration of the reactant A was at least ten-fold greater than that of the other reactant (reactant B) so that during the course of the reaction one can assume that reactant A's concentration essentially remains constant. The kinetic experiments carried out with both 10:1 and 1:10 dimethyldioxirane/alkene ratios, yielded k_2 values that were within experimental error of one another. GC-MS product studies showed the corresponding epoxide as the sole product for each case, respectively. All reactions were monitored for at least two half-lives. The epoxidation of *cis*- and *trans*-2-hexene by dimethyldioxirane yields the corresponding epoxides with retention of configuration as shown in reaction 4 and 5, respectively.



The results showed that the reaction was first order in dioxirane and alkene and second order overall, as expected. Representative linear pseudo first order plots are shown in Figure 9 and 10. The second order rate constants for the epoxidation of *cis*- and *trans*-2-hexene with the addition of other *cis*- and *trans*-alkenes that have been previously reported are listed in Table 1.

Jenson et al. contributed a valuable modeling study of the reaction of dimethyldioxirane attack with a pair of *cis*- and *trans*-alkenes.⁴⁶ Results showed that dimethyldioxirane approaches the *cis*-alkene from the less hindered side yielding a calculated value of 13.8 kcal/mol for the ΔE . While a higher activation of energy ($\Delta E = 17.2$ kcal/mol) was displayed when the dioxirane approached the *cis*-alkene on the most hindered side i.e. the side opposite of the hydrogen atoms. Hence, the side of the alkene with the least amount of alkyl groups is the most favored side for the dioxirane approach and one would not expect any major differences for *cis*-alkenes as the substituents increased in size. This correlates with the experimental results for the second order rate constants in Table 1. Thus the first four entries, **1** (methyl, $k_2 = 0.46 \pm 0.01 \text{ M}^{-1}\text{s}^{-1}$), **2** (ethyl, $k_2 = 0.46 \pm 0.01 \text{ M}^{-1}\text{s}^{-1}$), **3** (propyl, $k_2 = 0.50 \pm 0.01 \text{ M}^{-1}\text{s}^{-1}$), and **4** (isopropyl, $k_2 = 0.046 \pm 0.01 \text{ M}^{-1}\text{s}^{-1}$) did not show a significant difference in the second order rate constants whereas entry **5** (t-butyl, $k_2 = 0.26 \pm 0.02 \text{ M}^{-1}\text{s}^{-1}$) showed a slight decrease in reactivity. The later decrease in reactivity can be contributed to possible interactions of the lone pairs of the oxygen of the dioxirane with the t-butyl group of the alkene.

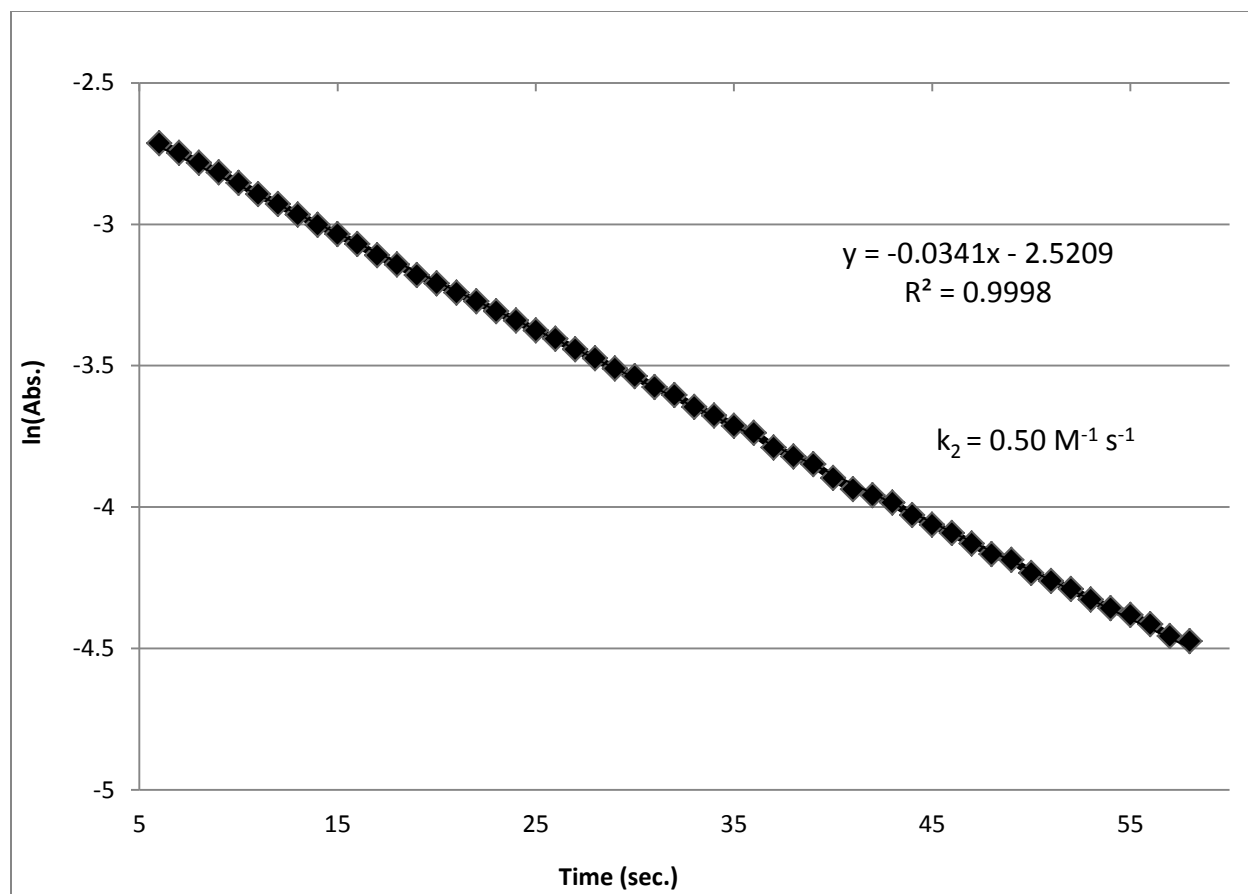


Figure 9. Pseudo first order plot of analyzed data of the epoxidation of *cis*-2-hexene by DMDO.

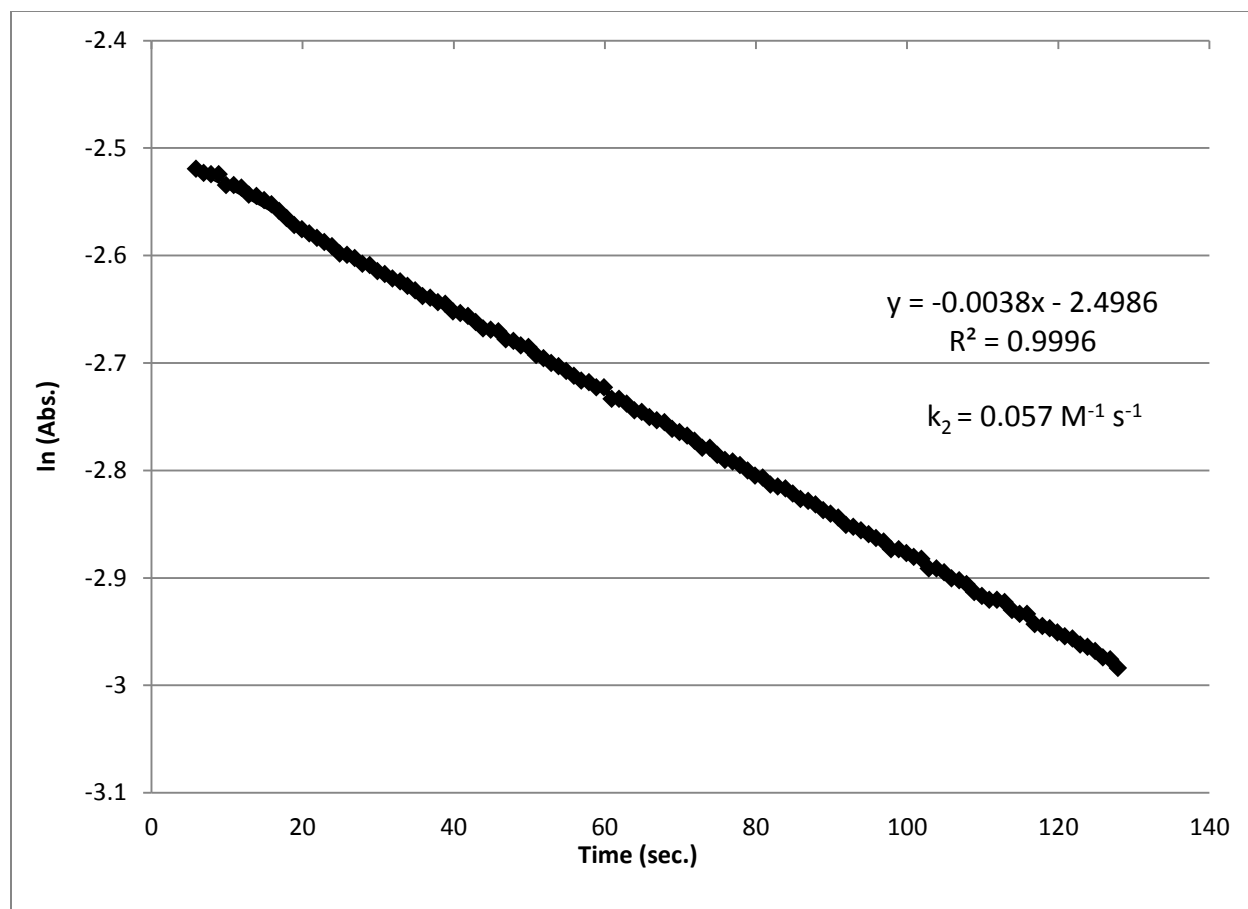
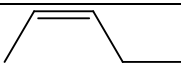

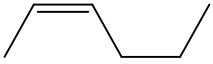
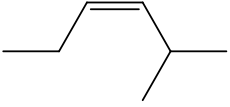
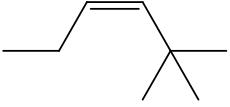
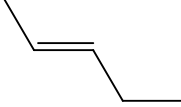
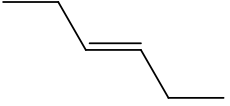
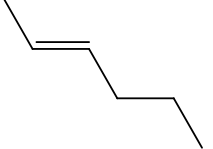
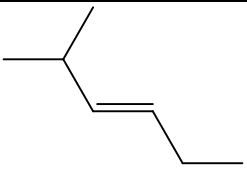
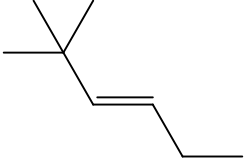


Figure 10. Pseudo first order plot of analyzed data of the epoxidation of *trans*-2-hexene by DMDO.

Table 1. Second order rate constants for the epoxidation of *cis*- and *trans*-alkenes series by DMDO in dried acetone at 330 nm and 23°C.

Entry	Alkene	k_2 (M ⁻¹ s ⁻¹)	k_2 cis/ k_2 trans
1		0.46 ± 0.01	7
2		0.46 ± 0.01^a	8
3		0.50 ± 0.01	9
4		0.46 ± 0.01^a	18
5		0.26 ± 0.02^a	22
6		0.070 ± 0.003^a	7
7		0.057 ± 0.004^a	8
8		0.057 ± 0.002	9
9		0.026 ± 0.002^a	18
10		0.012 ± 0.0012^a	22

a) Second order rate constants were previously recorded.^{11b,33}

Epoxidation of *trans*-alkenes by dimethyldioxirane show an appreciable decrease in the magnitude of the second order rate constants. The existence of two alkyl groups on either side of the alkene leads to a decrease in reactivity, since no matter the approach of dimethyldioxirane there will always be steric interactions present. Even for the smallest *trans*-alkene (*trans*-2-butene) with a predicted second order rate constant of $0.084 \pm 0.003 \text{ M}^{-1}\text{s}^{-1}$ shows a significant reaction difference compared to the *cis*-alkene. For the *trans*-isomers the second order rate constants decreased after the formal addition of each methyl group. For an example when comparing entries **6** and **7**, which only differ by the addition of a methyl group [one alkene has one methyl group and one ethyl group (**6**, $k_2 = 0.070 \pm 0.003 \text{ M}^{-1}\text{s}^{-1}$) while the other alkene has two ethyl groups (**7**, $k_2 = 0.057 \pm 0.004 \text{ M}^{-1}\text{s}^{-1}$)], the alkene with the methyl group (**6**) has a second order rate constant that is ~1.3 times faster than that for entry **7**. It can then be postulated that dimethyldioxirane approaches *trans*-alkenes on the less hindered side of the alkene similar to the *cis*-alkene i.e. the side where the alkyl group is the smallest and ultimately less sterically hindered. Compound **8**'s less sterically hindered group is a methyl group as well but possible steric interactions with the propyl group, that is free to rotate across its sigma bond, and that interaction with the lone pairs of the dioxirane can attribute to the lower reactivity of **8**, ($k_2 = 0.057 \pm 0.002 \text{ M}^{-1}\text{s}^{-1}$) towards dimethyldioxirane epoxidation. Consistent with the analysis compounds **9** and **10** have bulkier substituents (isopropyl and t-butyl groups) which cause increased steric interactions upon epoxidation by dimethyldioxirane, respectively. Thus the lower second order rate constants observed for compounds **9** ($k_2 = 0.026 \pm 0.002 \text{ M}^{-1}\text{s}^{-1}$) and **10** ($k_2 = 0.012 \pm 0.0012 \text{ M}^{-1}\text{s}^{-1}$) are of lower magnitude.

1.3.2 Computational modeling

Density Functional Theory 6-31G basis set. All calculations to study the mechanism of epoxidation by dimethyldioxirane were performed with the Density functional theory 6-31G basis set. The Density functional theory (DFT), allows one to calculate a variation of molecular properties including molecular structure, vibrational frequencies, atomization energies, ionization energies, electric and magnetic properties, and reaction paths. Density functional theory is a ground state theory which emphasizes the charge density as the most relevant physical measure. The advantage of using density functional theory is that no matter how large the system is DFT only using three variables to do the calculations (wave function of a N-electron system includes 3N variables). Semi-empirical (AM1) calculations are good for relative rate studies when there is no significant change in entropy between systems.⁴⁹

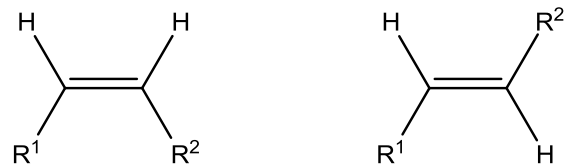
Computational Methods. DFT calculations were performed on the Spartan version'10 software for the epoxidation of two series of seven *cis*-/*trans*-alkene pairs (Figure 11) by dimethyldioxirane. The seven *cis*-/*trans* alkenes (**2-cis/ 2-trans** – **8-cis/ 8-trans**) can be considered as two series. The first series was *cis*-/*trans*-2-butene (**2-cis/2-trans**), *cis*-/*trans*-2-hexene (**3-cis/3-trans**), *cis*-/*trans*-4-methyl-2-pentene (**4-cis/4-trans**), and *cis*-/*trans*-4,4-dimethyl-2-pentene (**5-cis/5-trans**), where the number of branching alkyl groups increase (0,1,2,3, respectively) along the series while the other group (methyl) remained constant. The second series contained *cis*-/*trans*-3-hexene (**6-cis/6-trans**), *cis*-/*trans*-4-methyl-3-hexene (**7-cis/7-trans**), *cis*-/*trans*-4,4-dimethyl-3-hexene (**8-cis/8-trans**), which all have an ethyl group as a constant and the size and branching of the second substituent is increasing (1,2,3, respectively).

The ground state energies were first calculated for every reactant and product (Table 2). Energy profile calculations were complete for every reactant to ensure that the localized minima

were met. The optimized reactants (alkenes and dimethyldioxirane) were merged together and oriented to mimic the possible orientation of the epoxidation as described in Figure 12.

Table 2. Optimized ground state energies of reactants for computational modeling of DMDO epoxidations.

Compound	Ground State Energy (Hartrees)	Ground State Energy (<i>kcal/mol</i>)
<i>cis</i> -2-butene	-157.224765	-98658.54
<i>trans</i> -2-butene	-157.226964	-98659.92
<i>cis</i> -2-hexene	-235.851809	-147997.01
<i>trans</i> -2-hexene	-235.854343	-147998.60
<i>cis</i> -3-hexene	-235.851522	-147996.83
<i>trans</i> -3-hexene	-235.853944	-147998.35
<i>cis</i> -2-methyl-3-hexene	-275.165705	-172666.48
<i>trans</i> -2-methyl-3-hexene	-275.168239	-172668.07
<i>cis</i> -4-methyl-2-pentene	-235.852335	-147997.34
<i>trans</i> -4-methyl-2-pentene	-235.853498	-147998.07
<i>cis</i> -2,2-dimethyl-3-hexene	-314.473020	-197331.82
<i>trans</i> -2,2-dimethyl-3-hexene	-314.480861	-197336.74
<i>cis</i> -4,4-dimethyl-2-pentene	-275.158311	-172661.84
<i>trans</i> -4,4-dimethyl-2-pentene	-275.167235	-172667.44
dimethyldioxirane	-268.268908	-168338.74



$R^1 = R^2 = \text{Me}$ **2-*cis*, 2-*trans***

$R^1 = \text{Me}; R^2 = \text{n-Pro}$ **3-*cis*, 3-*trans***

$R^1 = \text{Me}; R^2 = \text{i-Pro}$ **4-*cis*, 4-*trans***

$R^1 = \text{Me}; R^2 = \text{t-Butyl}$ **5-*cis*, 5-*trans***

$R^1 = R^2 = \text{Et}$ **6-*cis*, 6-*trans***

$R^1 = \text{Et}; R^2 = \text{i-Pro}$ **7-*cis*, 7-*trans***

$R^1 = \text{Et}; R^2 = \text{t-Butyl}$ **8-*cis*, 8-*trans***

Figure 11. The structures of *cis/trans* pairs of alkenes for the DFT computational modeling.

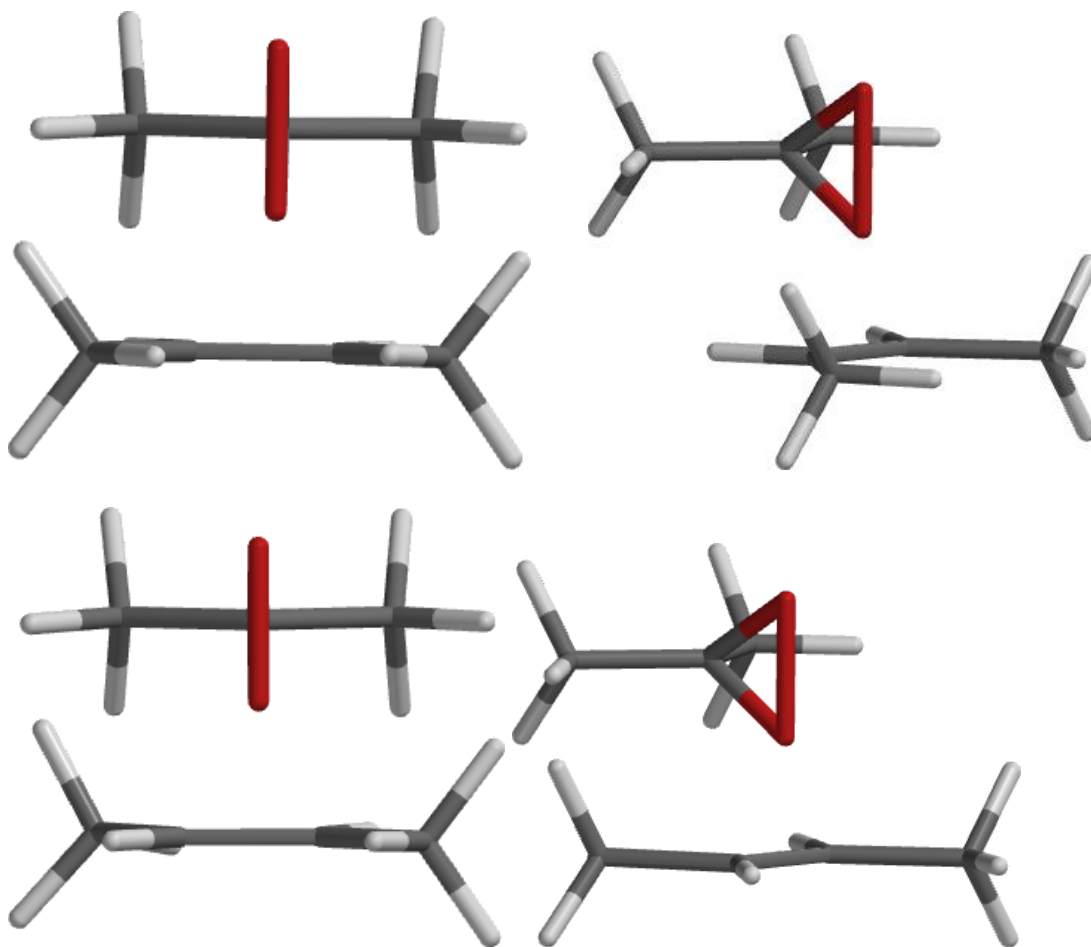


Figure 12. Geometry optimized structures of DMDO and *cis*-2-butene (**2-*cis***) merged together in preparation for DMDO epoxidation.

Transition state calculation. The optimized structures of the reactants were arranged to begin the oxygen insertion step. A transition state guess was implemented by displaying an electrophilic process showing electrons transferring from the double bond of the alkene to the oxygen atom of dimethyldioxirane (Figure 13). Upon achieving an agreeable “weak complex” (Figure 14), the calculation is carried out.

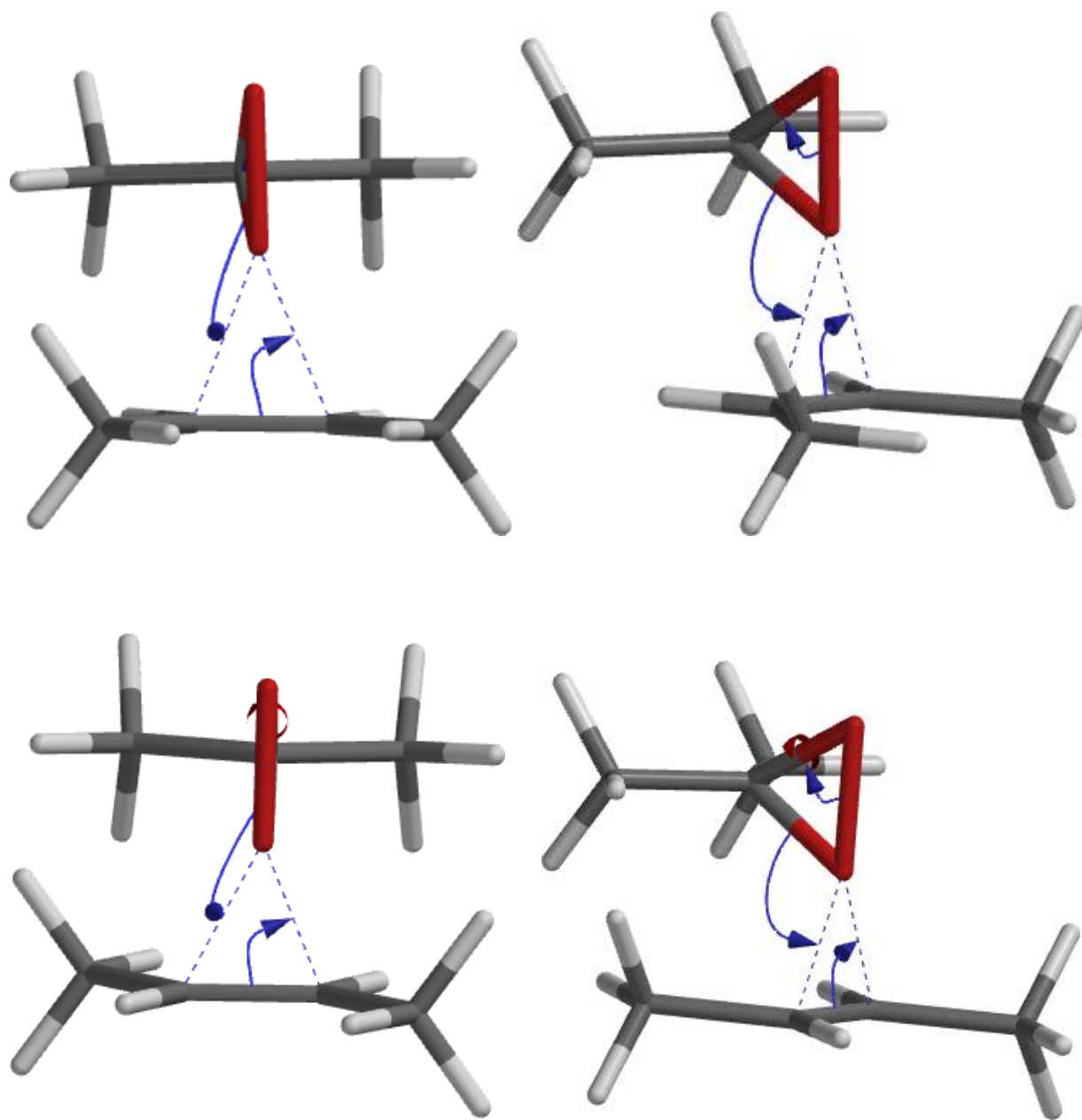


Figure 13. Transition state guess input of *cis*-2-butene (top two figures) and *trans*-2-butene (bottom two figures) epoxidation by DMDO.

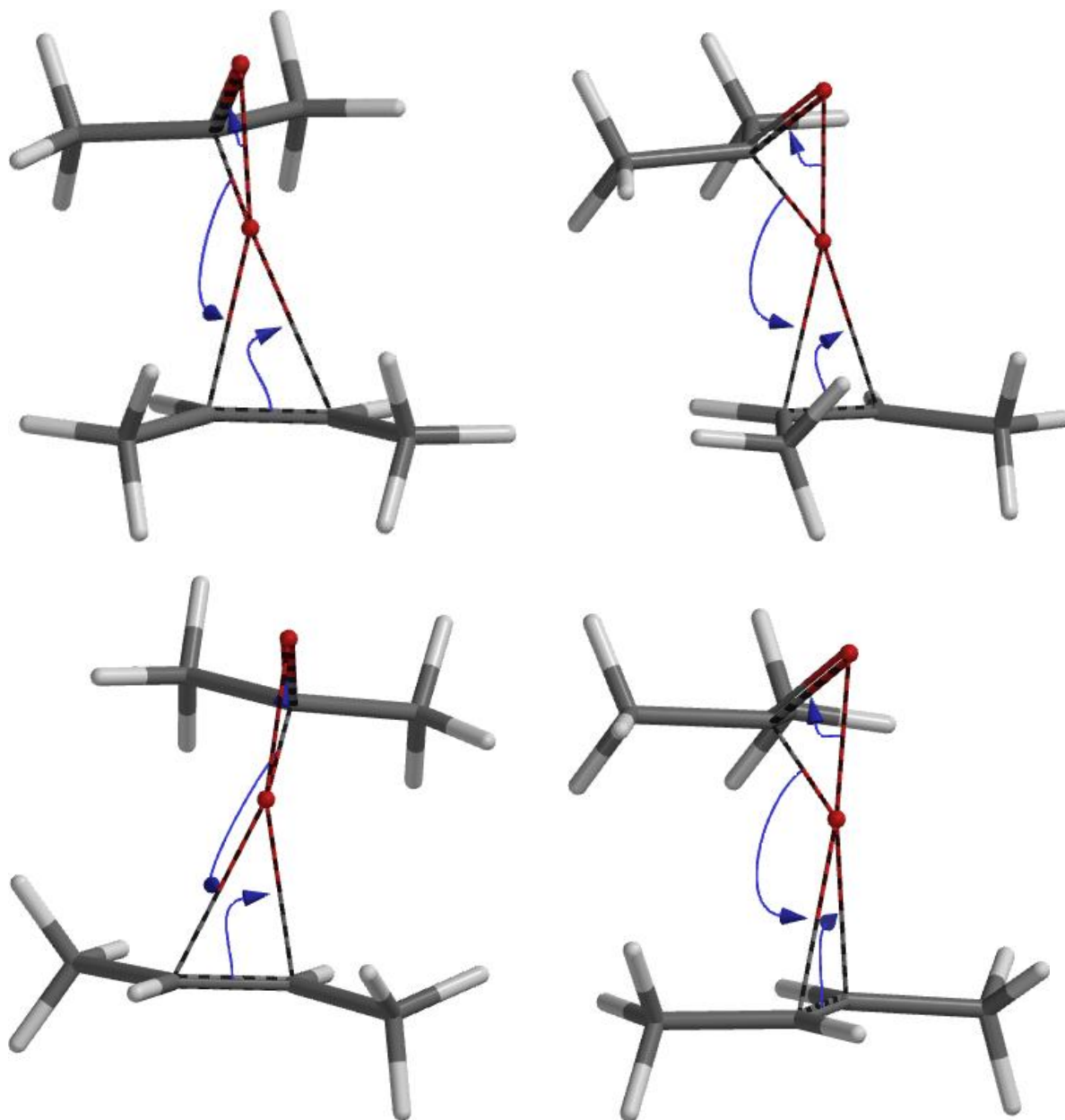


Figure 14. Transition state guess "weak complex" of *cis*-2-butene (top two figures) and *trans*-2-butene (bottom two figures) epoxidation by DMDO.

DFT calculated bond lengths and imaginary frequencies were determined for each series of *cis*-/*trans*-alkenes. The data are presented in Table 3 for the *cis* alkenes and Table 4 for the *trans* alkenes. The bond lengths and imaginary frequencies do not show a significant difference within the *cis* compounds as the structures changes. Bond numbers 2 and 3 are essentially the same for each *cis* epoxidation with only a slight difference in bonds numbers 2 and 3 of **8-cis** which can be attributed to the larger substituent of **8-cis**. Though overall, the bond lengths for the *cis* epoxidation transition states correspond to an ideal symmetrical synchronous spiro geometry.

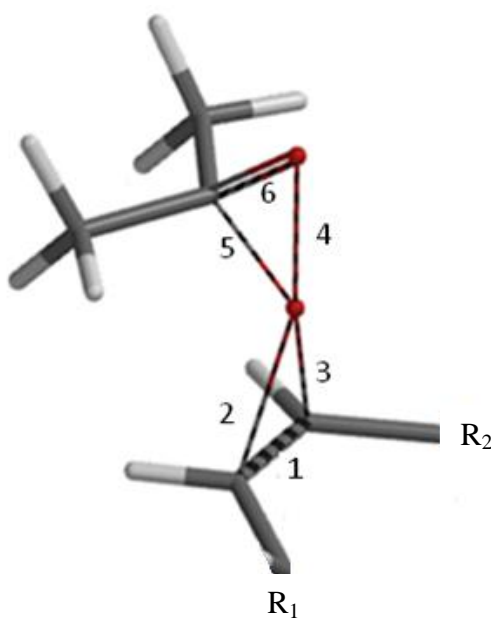


Table 3. Calculated bond lengths (Å) and imaginary frequencies (μ , cm^{-1}) for the transition states (TS) for 2-*cis*-8-*cis* epoxidation.

Bond number	TS- <i>cis</i> -Alkene							
	2- <i>cis</i>		3- <i>cis</i>	4- <i>cis</i>	5- <i>cis</i>	6- <i>cis</i>	7- <i>cis</i>	8- <i>cis</i>
1	1.380	(1.380 ^a)	1.380	1.380	1.381	1.380	1.379	1.381
2	2.023	(2.026 ^a)	2.033	2.034	2.048	2.029	2.042	2.084
3	2.026	(2.026 ^a)	2.021	2.040	2.043	2.024	2.040	2.022
4	1.886	(1.886 ^a)	1.883	1.879	1.876	1.883	1.875	1.873
5	1.487	(1.485 ^a)	1.485	1.484	1.482	1.485	1.481	1.482
6	1.327	(1.327 ^a)	1.327	1.329	1.330	1.327	1.330	1.331
$\mu(\text{cm}^{-1})$	464	(466.7 ^a)	464	443	441	462	440	435

a) From reference 44.

Contrastingly, bond lengths 2 and 3 displayed in Table 4 for the transition state geometries of the *trans* compounds are varied. There is around a 0.200 Å difference between bond numbers 2 and 3. The values are consistent with an asynchnous asymmetrical spiro transition state with a tilt away from the applied steric interactions developed by the R₁.

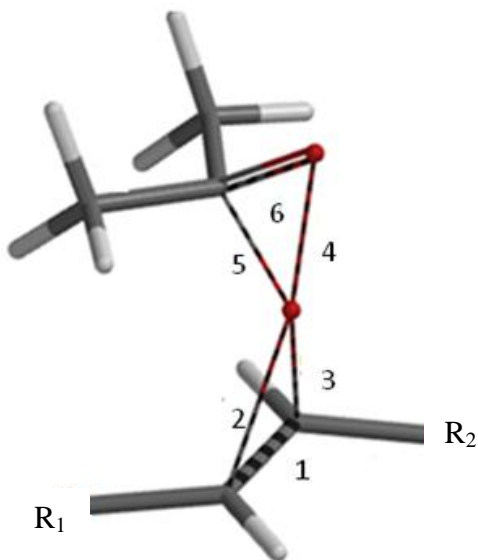


Table 4. Calculated bond lengths (Å) and imaginary frequencies (μ , cm^{-1}) for the transition states (TS) for 2-*trans*-8-*trans* epoxidation.

Bond number	<i>TS-trans-Alkene</i>							
	<i>2-trans</i>		<i>3-trans</i>	<i>4-trans</i>	<i>5-trans</i>	<i>6-trans</i>	<i>7-trans</i>	<i>8-trans</i>
1	1.378	(1.378 ^a)	1.378	1.378	1.377	1.378	1.378	1.376
2	2.137	(2.140 ^a)	2.133	2.136	2.154	2.145	2.129	2.141
3	1.937	(1.935 ^a)	1.943	1.951	1.968	1.936	1.956	1.978
4	1.883	(1.883 ^a)	1.883	1.881	1.871	1.880	1.882	1.869
5	1.496	(1.494 ^a)	1.495	1.494	1.488	1.493	1.496	1.489
6	1.328	(1.325 ^a)	1.325	1.326	1.330	1.326	1.326	1.330
$\mu(\text{cm}^{-1})$	484	(479.7 ^a)	477	470	447	471	474	445

a) From reference 44.

Verification of the transition state. Once the transition state was located from the DFT B3LYP calculation it was important to confirm the authenticity mathematically and to confirm that it corresponded to the reaction process. The verification that the transition state was mathematically correct was done by checking the imaginary frequency of the transition state. The Hessian matrix gave one and only one imaginary frequency for each transition state calculation. Representative values for imaginary frequencies range from 300-200 cm^{-1} . To ensure the transition state corresponded to the epoxidation process, an intrinsic reaction coordinate calculation (IRC) was carried out (Figure 15). The calculation began at the transition state (saddle point) and followed a path to the reactants and products of the epoxidation. The IRC animation connected two minima points on the potential energy surface by a route that passed through the transition state between them. The IRC profiled a classic concerted exothermic reaction, displaying a nucleophilic attack of the electrons of the double bond to the oxygen of the dioxirane. The IRC shows a continuous increase in energy from starting materials to the transition state and then a continuous decrease in energy from transition state to products.

Electronic activation energies and relative rates calculation. Electronic activation energies were calculated by subtracting the ground state energies of the starting materials from that of the transition state, as described as follows:

$$\Delta E_a = (\text{Transition state energy} - \text{Ground state energy reactants})$$

As listed in Tables 5-11 the electronic activation energies for the *cis* compounds are always less than those of the analogous *trans* isomers. These calculations are consistent with our

experimental results which showed that the *cis* compounds are more reactive than the *trans* compounds.

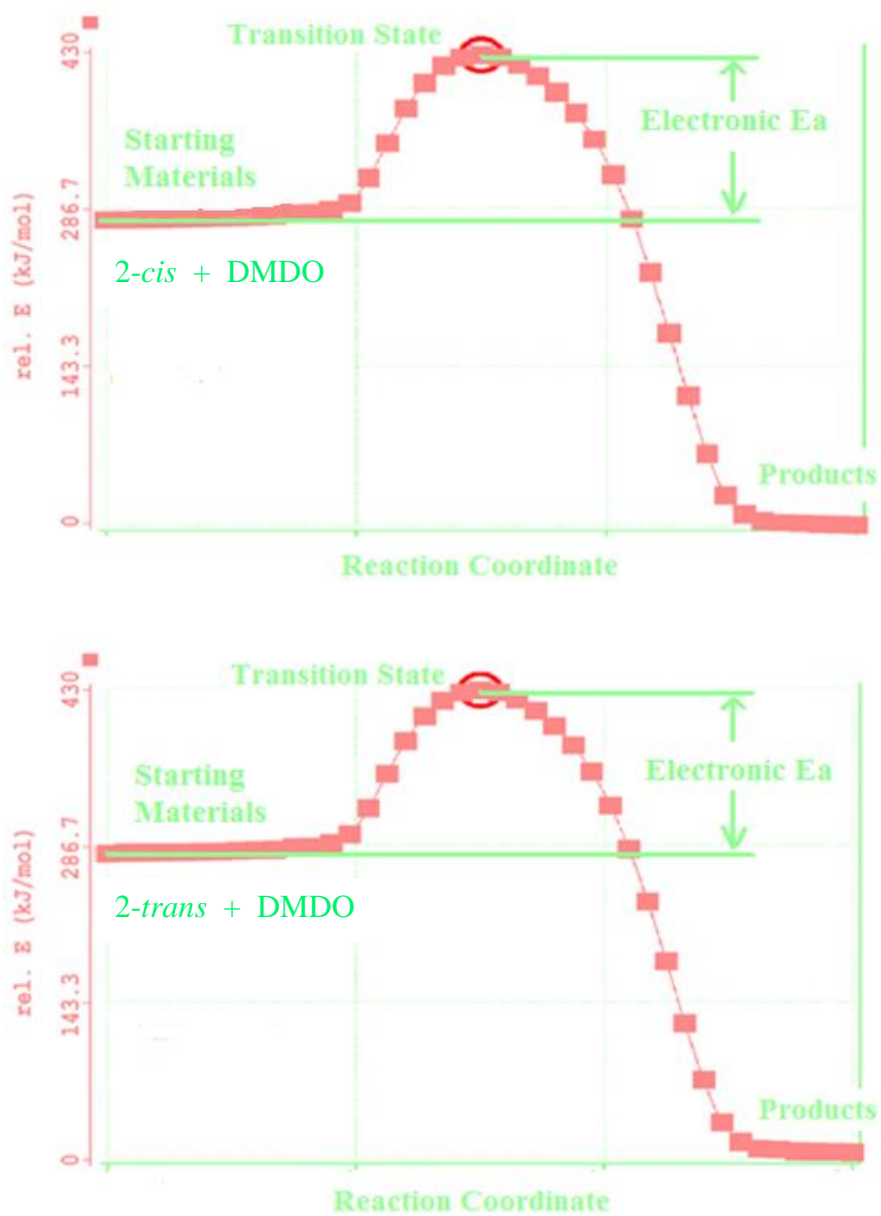


Figure 15. Reaction coordinate profile for the epoxidation of **2-cis** and **2-trans** by DMDO.

Table 5. DFT calculated electronic energies (gas phase) for the epoxidation of *cis*-/*trans*-2-butene by DMDO at 23°C.

System	Ground State Energy (kcal/mol)	Transition State Energy (kcal/mol)	Activation Energy (kcal/mol)
[<i>cis</i> -2-butene + DMDO]	-266997.28	-266983.36	13.92
[<i>trans</i> -2-butene +DMDO]	-266998.66	-266983.16	15.50

Table 6. DFT calculated electronic activation energies (gas phase) for epoxidation of *cis*-/*trans*-2-hexene by DMDO at 23°C.

System	Ground State Energy (kcal/mol)	Transition State Energy (kcal/mol)	Activation Energy (kcal/mol)
[<i>cis</i> -2-hexene + DMDO]	-316335.75	-316322.03	13.85
[<i>trans</i> -2-hexene +DMDO]	-316337.34	-316321.90	15.44

Table 7. DFT calculated electronic activation energies (gas phase) for the epoxidation of *cis*-/*trans*-3-hexene by DMDO at 23°C.

System	Ground State Energy (kcal/mol)	Transition Energy (kcal/mol)	State Activation Energy (kcal/mol)
[<i>cis</i> -3-hexene + DMDO]	-316335.57	-316321.61	13.96
[<i>trans</i> -3-hexene +DMDO]	-316337.09	-316321.78	15.31

Table 8. DFT calculated activation energies for the epoxidation of *cis*-/*trans*-2-methyl-3-hexene by DMDO at 23°C.

System	Ground State Energy (kcal/mol)	Transition Energy (kcal/mol)	State Activation Energy (kcal/mol)
[<i>cis</i> -2-methyl-3-hexene + DMDO]	-341005.22	-340991.96	13.26
[<i>trans</i> -2-methyl-3-hexene +DMDO]	-341006.81	-340991.14	15.67

Table 9. DFT calculated activation energies for the epoxidation of *cis*-/*trans*-4-methyl-2-pentene by DMDO at 23°C.

System	Ground State Energy (kcal/mol)	Transition Energy (kcal/mol)	State Activation Energy (kcal/mol)
[<i>cis</i> -4-methyl-2-pentene +DMDO]	+ -316336.08	-316322.91	13.17
[<i>trans</i> -4-methyl-2-pentene +DMDO]	-316336.81	-316321.86	14.95

Table 10. DFT calculated activation energies for the epoxidation of *cis*-/*trans*-2,2-dimethyl-3-hexene by DMDO at 23°C.

System	Ground	State	Transition	State	Activation
	Energy		Energy		Energy
	(kcal/mol)		(kcal/mol)		(kcal/mol)
[<i>cis</i> -2,2-dimethyl-3-hexene	+ -365670.56		-365657.48		12.95
DMDO]					
[<i>trans</i> -2,2-dimethyl-3-hexene	-365675.48		-365660.86		15.48
+DMDO]					

Table 11. DFT calculated activation energies of epoxidation of *cis*-/ *trans*-4,4-dimethyl-2-pentene by DMDO at 23°C.

System	Ground	State	Transition	State	Activation
	Energy		Energy		Energy
	(kcal/mol)		(kcal/mol)		(kcal/mol)
[<i>cis</i> -4,4-dimethyl-2-pentene	+ -341000.58		-340988.26		12.32
DMDO]					
[<i>trans</i> -4,4-dimethyl-2-pentene	-341006.18		-340991.68		14.50
+DMDO]					

The electronic activation energies were compared to the experimental results in Table 12. As expected (previously recognized), the electronic activation energies are significantly higher than the experimental values but followed the same trends.⁴²⁻⁴⁶ For the first series **2-cis/2-trans** to **5-cis/5-trans** the ΔE_{a} s are considerably consistent (~1.5-1.7) with the exception of 5-cis/5-trans which has a larger ΔE_{a} value (-2.2). This exception may be due to the larger t-Bu groups which are the largest R-groups of the series. The second series where one has a consistent ethyl group on one side of every alkene and an increasing methyl group for the other shows an increase in the activation energies as the R₂ group increases in size becoming more branched. Though there is an overestimation for the electronic activation energies, the experimental $\Delta\Delta H^\ddagger$ are still in reasonable agreement with the electronic activation energies.

Table 12. Comparison of the electronic activation energies of the epoxidation of **2-cis/2-trans-8-cis/8-trans** by DMDO vs. the experimental values.

Alkene	Electronic Ea	Electronic ΔE_a^a	Experimental ΔH^\ddagger	Experimental $\Delta\Delta H^\ddagger$
2-cis	13.87 (13.8 ^b , 13.85 ^c)	-1.65 (-1.7 ^b) (-1.65 ^c)	N/A ^d	N/A ^d
2-trans	15.52 (15.5 ^b , 15.50 ^c)		N/A ^d	N/A ^d
3-cis	13.72	-1.54	NR ^e	NR ^e
3-trans	15.26			
4-cis	14.24	-1.58	7.28	-2.1±0.4
4-trans	15.82		9.42	
5-cis	12.32	-2.18	7.37	-1.9±1.0
5-trans	14.50		9.27	
6-cis	13.96	-1.35	7.14	-1.1±1.1
6-trans	15.31		8.25	
7-cis	13.26	-2.41	7.92	-2.0±0.4
7-trans	15.67		9.92	
8-cis	12.95	-2.53	7.51	-2.0±0.9
8-trans	15.48		9.47	

a) Electronic Ea for the epoxidation of the cis isomer minus the electronic Ea for the epoxidation of the trans isomer b) Data from reference 46 c) Data from reference 44 d) No data available since *cis-/trans*-2-butene are gases at ambient temperatures. e) Only kinetic studies were carried out.

Electronic relative rates for the epoxidations for the series of alkenes (**2-cis/2-trans-8-cis/8-trans**) were estimated from the Density Functional Theory B3LYP basis set. Electronic relative rates can be estimated from the electronic activation energies as follows:

$$k_2 = A e^{-(\Delta E_a - RT)}$$

where A = Pre-exponential factor (frequency factor)

$$\Delta E_a = E_{a \text{ cis isomer}} - E_{a \text{ trans isomer}}$$

R = Gas constant

T = Temperature (Kelvin)

Based on the assumption that there is no substantial difference in the reaction organization for the epoxidation of each alkene by dimethyldioxirane, the frequency factor (A) can be canceled out to allow the calculation of the relative reactivities. The electronic relative reactivities for each cis-/trans- pair is displayed in Table 13 along with the experimental values. There is reasonable agreement as to the trend in each series but the calculations overestimate the reactivity differences for the bulkier substituents.

Table 13. DFT electronic relative reactivities of the epoxidation of **2-cis/2-trans** - **8-cis/8-trans** by DMDO vs. experimental values.

Alkene Pair	2-cis/ 2-trans	3-cis/ 3-trans	4-cis/ 4-trans	5-cis/ 5-trans	6-cis/ 6-trans	7-cis/ 7-trans	8-cis/ 8-trans
Electronic relative $k_{2\text{-cis}}/k_{2\text{-trans}}$	16/1	13/1	14/1	41/1	10/1	57/1	74/1
Normalized experimental $k_{2\text{-cis}}/k_{2\text{-trans}}$	N/A	8.8/1	8.8/1	14/1	8.2/1	11/1	22/1

The electronic activation energies for the epoxidation for the *cis* compounds were relatively the same until a larger (bulkier) R-group was present. For example the electronic activation energies for the *cis* compounds remained around 13 kcal/mol and only increased if there was a larger substituent present as in the case of **4-cis** with electronic activation energy of 14.24. The

electronic activation energies for the epoxidation of the *trans* isomers seemed relatively consistent predicting a slower reactivity than the corresponding *cis* compounds. Data show that the assumption that the ΔS^\ddagger was essentially constant for each *cis* and *trans* pair yielded correct trends in reactivity but yield overestimation of the differences when the substituents became larger.

1.4 Conclusions

- DMDO is conveniently prepared from commercially available materials to afford up to 0.1 M isolated DMDO solutions in acetone (stable at -20°C until use).
- Kinetic studies with isolated dimethyldioxirane showed that *cis*-2-hexene underwent epoxidation faster than *trans*-2-hexene, consistent with previously DMDO epoxidation relative reactivities.
- Basic Density Functional Theory calculations using the 6-31 G basis set correctly predicted the relative reactivities of two series of *cis*-/*trans*-alkenes epoxidations by dimethyldioxirane.
- The predicted DFT transition state geometry was in a relatively symmetrical and spiro-transition state, independent of the size of the alkyl groups for the *cis*-alkenes and an asymmetrical asynchronous spiro geometry with a tilt, tilting away from the *trans*-alkene's substituent. The tilt becomes more exaggerated as the size of the substituent increases.
- DFT calculated lower electronic Eas for the *cis*-alkenes compared to those of the *trans*-alkenes which is consistent with the greater reactivity of the *cis*-alkenes towards epoxidation by dimethyldioxirane.

- Prediction of relative k_{cis}/k_{trans} based on the electronic Eas was in reasonable agreement with experimental values but greatly overpredicted the value for the t-Bu containing pairs.
- Overall, the DFT approach is a reliable method to model this type of reaction and for predicting relative reactivities.

1.5 References

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1.6 Published work

Postscript. This work has been published in Heterocyclic Communications Title: The reaction of dimethyldioxirane with 1,3-cyclohexadiene and 1,3-cyclooctadiene: monoepoxidation kinetics and computational modeling.

Author(s): McTush-Camp, Davita; Vasquez, Pedro C.; Baumstark, Alfons L.

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Davita McTush-Camp was responsible for all kinetics and computational modeling under the mentoring of Dr. Alfons Baumstark. The manuscript was written by Davita McTush-Camp under mentoring of Dr. Alfons Baumstark. Dr. Pedro Vasquez is the laboratory manager for the Baumstark research group and handles laboratory upkeep and safety guidelines.

Statement of Research

Baumstark and Chen reported kinetic data for the monoepoxidation of *s-trans* acyclic conjugated dienes by dimethyldioxirane. It was found that the rate of monoepoxidation is less sensitive to structural effects and *cis*-/ *trans*- substitution than that for the epoxidation of simple aliphatic alkenes by dimethyldioxirane. The primary aim for this work is to study the monoepoxidation of *s-cis* cyclic conjugated dienes by DMDO. The kinetic and computational study of the monoepoxidation of 1,3-cyclohexadiene and 1,3-cyclooctadiene will be carried out to determine if structural effects will affect the rate of epoxidation. Computational methodologies will be employed to model the experimental data. This should provide insights into the factors that affect the reactivity in these systems.

**The reaction of dimethyldioxirane with 1,3-cyclohexadiene and 1,3-cyclooctadiene:
monoepoxidation kinetics and computational modeling**

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Abstract.

The reaction of dimethyldioxirane (**1**) with excess 1,3-cyclohexadiene (**2a**) and 1,3-cyclooctadiene (**2b**) in dried acetone yielded the corresponding monoepoxides in excellent yield. Second-order rate constants for monoepoxidation were determined using UV methodology. The k_2 value for the monoepoxidation of 1,3-cyclohexadiene was found to be $1.14 \pm 0.06 \text{ M}^{-1} \text{ s}^{-1}$, whereas that for the monoepoxidation of 1,3-cyclooctadiene was $0.31 \pm 0.03 \text{ M}^{-1} \text{ s}^{-1}$. Basic density functional calculations at the B3LYP/6-31G level were employed to model the monoepoxidations. As expected, the calculations were consistent with a concerted, electrophilic process with a spiro-transition state. As found for the epoxidation of simple alkenes, the calculated transition-state geometry showed a slight asynchronous tilt of the dioxirane plane relative to that of the remaining alkene portion of the diene and a slight tilt back from the face of the diene. Relative reactivities (relative k_2 values) were determined using the difference in the calculated electronic activation energies and were consistent with the experimental relative k_2 values without the need to correct for the medium (solvent). Reactivity differences for epoxidation can be quickly predicted by this approach as long as there are reasonable structural similarities between the substrates.

Keywords: density functional theory (DFT) calculations; dimethyldioxirane; epoxidation; kinetics.

Introduction

Studies have shown dioxiranes to be powerful oxidants [1–4]. Dimethyldioxirane (**1**), in particular, has been useful in carrying out many synthetic transformations, adding an oxygen to a variety of substrates [1–4]. One of the most studied reactions of **1** is the epoxidation of olefins. Dimethyldioxirane epoxidations have been shown to be sensitive toward steric and substituent effects [1–4]. Kinetic studies have shown the relative reactivities for *cis* vs. *trans* epoxidation by **1** of simple alkyl substituted alkenes to be approximately 8:1 or greater [5]. The reverse reactivity trend for the epoxidation of phenyl-substituted alkenes was noted as the major exception [6]. However, all epoxidations by **1** have been shown to be quantitative and stereospecific. Mechanistically, the epoxidations have been postulated to occur via a spiro-transition state [1–7]. Semiempirical (AM1) calculations have been shown to be useful in modeling dimethyldioxirane epoxidation of simple alkenes within a structurally homologous series [8]. Density functional theory (DFT) calculations were used to model the epoxidation of ethylene, propene, and *cis*- and *trans*-2-butene by both the parent unsubstituted dioxirane and **1** and predicted a spiro-transition state in agreement with the mechanism postulated based on experimental data [9–12]. Ab initio calculations, employed to model *cis* and *trans* epoxidations by **1** also predicted a spiro-transition state and the correct relative reactivity of *cis* vs. *trans* simple alkenes [13]. Semiempirical (AM1) calculations failed to predict the relative reactivities of the epoxidation of alkenes by **1** within a series in which there were only minor reactivity differences as well as across two series for which there are small reactivity differences [14]. Basic gas phase DFT calculations proved to be effective for modeling the epoxidation of α,β -unsaturated esters by **1** as well as for the epoxidation of several acyclic conjugated dienes (*s-trans* systems) by dioxirane, systems for which steric effects are minimized [15, 16]. No

studies have been reported for the epoxidation of cyclic conjugated *s-cis* dienes. We report here the results of a kinetic study with computational modeling of the epoxidation of 1,3-cyclohexadiene (**2a**) and 1,3-cyclooctadiene (**2b**) by dimethyldioxirane (**1**).

Results and Discussion

The reaction of **1** with excess 1,3-cyclohexadiene (**2a**) and 1,3-cyclooctadiene (**2b**) were carried out in dried acetone (Scheme 1). Under these conditions, the monoepoxide was the major product in either case. The monoepoxides were isolated in low yield and characterized by ¹H NMR and GC-MS data. The spectroscopic data were in agreement with the literature values [17]. Kinetic studies with **2a** and **2b** were carried out using UV methodology in dried acetone at 23°C. The epoxidations by **1** were shown to be of the first order in dioxirane and in diene; second-order overall. 1,3-Cyclohexadiene was found to be more reactive toward monoepoxidation than 1,3-cyclooctadiene. Pseudo-first-order conditions with a 10:1 diene/dioxirane ratio were employed to determine the k_2 value for the monoepoxidation of 1,3-cyclooctadiene. Owing to the greater reactivity, second-order conditions were employed to determine the k_2 value for the monoepoxidation of 1,3-cyclohexadiene. Representative plots of the kinetic data are shown in Figures 1 and 2. The k_2 values for the monoepoxidation of 1,3-cyclohexadiene and 1,3-cyclooctadiene are 1.14 ± 0.06 and 0.31 ± 0.03 m⁻¹ s⁻¹, respectively. The k_2 value for the monoepoxidation of 1,3-cyclohexadiene is comparable to those for the monoepoxidation of disubstituted acyclic conjugated dienes (1.29–1.42 m⁻¹ s⁻¹) by **1** [14]. The k_2 value for the monoepoxidation of 1,3-cyclooctadiene is comparable to that for the epoxidation of simple *cis*-alkenes by **1** [8].

The monoepoxidations of the cyclic dienes were modeled by applying a basic DFT approach using the B3LYP/6-31G basis set. Regardless of the initial orientation of the reactants,

minimized transition-state calculations yielded a spiro-transition state with a slight asynchrony tilt for the monoepoxidation of in Figure 3. The calculated transition-state geometries for these cases are consistent with previous results for the epoxidation of simple alkenes by **1**, which also show similar asymmetry and tilts for the spiro-transition states [9–14]. The basic DFT approach was employed to quickly predict relative reactivities. These calculations were carried out in the gas phase because solvent corrections have been shown to lower the individual values but not affect the difference between values [18]. The predicted activation energies were determined by taking the difference between the calculated energies of the transition state and those of the ground states of the reactants while controlling for conformational effects. The predicted activation energies for 1,3-cyclohexadiene and 1,3-cyclooctadiene were found to be 13.37 and 14.14 kcal, respectively. The k_{rel} predicted values were calculated from the electronic activation energy difference for the two cyclic dienes. The ground-state geometry calculations of 1,3-cyclohexadiene and 1,3-cyclooctadiene show that 1,3-cyclohexadiene resembles a relatively flat *s-cis* system. The ground-state structure of the 1,3-cyclooctadiene shows the two double bonds to have a torsion angle of 51°, reducing conjugation. The predicted relative rates for **2a/2b** of 3.9: 1 are consistent with the experimental kinetic data for **2a/2b** of 3.7:1. The kinetic and predicted data are shown in Table 1. The HOMO-LUMO energies were taken from the DFT B3LYP 6-31G optimized geometries of 1,3-cyclohexadiene, 1,3-cyclooctadiene, and dimethyldioxirane. The HOMO energies of 1,3-cyclohexadiene and 1,3-cyclooctadiene are -5.59 and -6.05 eV, respectively. The LUMO energy of dimethyldioxirane is -0.47 eV. These data are consistent with the DFT results predicting that the 1,3-cyclohexadiene would be more reactive than the 1,3-cyclooctadiene. On the basis of the successful modeling of the cyclic dienes, the relative rate constants for *cis-/trans*-phenyl- substituted alkenes **4a,b** were evaluated using this quick, gas-

phase calculation method. The transition-state geometries of the epoxidation of *cis*-1-phenylpropene and *trans*-1-phenylpropene by **1** were determined (Figure 4). The second-order rate of the epoxidation of *cis*-1-phenylpropene and *trans*-1-phenylpropene by **1** (Scheme 2) have been previously reported as 0.18 ± 0.01 and 0.29 ± 0.02 , respectively, and noted as an exception of the overall trend of the reactivity of epoxidation by **1** of *cis* vs. the corresponding *trans*-alkene [6]. As expected, the calculation predicted that the epoxidation occurs *via* a concerted, electrophilic process with a spiro-transition state including a slight asynchrony tilt in the oxygen insertion bond formation. The electronic activation energies for the epoxidation of *cis*-1-phenylpropene and *trans*-1-phenylpropene were determined to be 14.00 and 13.80 kcal, respectively. The calculated relative reactivity was calculated to be 1.2:1, *trans*-1-phenylpropene/*cis*-1-phenylpropene, whereas the experimental relative reactivity was 1.6:1, thus successfully predicting the greater reactivity of the *trans* isomer. Table 2 summarizes the electronic and experimental data. The DFT results show that the exception in relative reactivity for **4a** and **4b** is actually consistent with the steric effect argument, but in this case, the *trans* isomer has the least steric interactions leading to the apparent reversal.

Conclusions

1,3-Cyclohexadiene (**2a**) was found to be more reactive than 1,3-cyclooctadiene toward monoepoxidation by **1**. Kinetic studies showed that the overall reactivity for the monoepoxidation of the essentially *s-cis* 1,3-cyclohexadiene is comparable to that of the *s-trans* acyclic conjugated dienes with similar number of substituents. The results of the study of the less reactive substrate, 1,3-cyclooctadiene (**2b**), are similar to the second-order rate constants of simple *cis*-alkenes. It appears that the two double bonds behave as if they are isolated alkenes for this case. Basic DFT calculations (gas phase) are consistent with the concerted (spiro)

mechanism for the monoepoxidation of the dienes and predicted the relative reactivity with reasonable agreement with experimental data. Application of this approach to epoxidation of *cis*-/*trans*-1-phenylpropene successfully predicted the previously noted unexpected reactivity for this pair of alkenes. The method appears to be able to detect the effect of subtle steric interactions in these closely related systems. The basic DFT method is a reliable quick approach to model dioxirane epoxidation reactions and for predicting relative reactivities as long as the reactants have reasonable structural similarities and conformational factors are controlled without the need for time consuming solvent corrections. The challenge of predicting the relative reactivities for substrates with vast structural differences toward epoxidation by **1** still remains to be addressed.

Experimental

Dimethyldioxirane was prepared by the general procedure developed by Murray, for the reaction of oxone and acetone, with modifications [5, 7]. Stock solutions (≤ 0.1 M in acetone) were collected by redistillation of the initial azeotrope [1–4]. The dimethyldioxirane concentration in acetone was determined using UV methodology (λ 330 nm and molar absorptivity of 12.9 cm⁻¹ m⁻¹) [6]. Dimethyldioxirane stock solutions were stored at -20°C over anhydrous Na₂SO₄ until use. Stock solutions were stable for months under these conditions. 1,3-Cyclohexadiene and 1,3-cyclooctadiene were commercially available and were distilled before use. Stock solutions of the dienes in dried acetone were prepared under anhydrous Na₂SO₄ at room temperature and used the same day. For kinetic runs, the temperature of the jacketed sample cell (23.0±0.3°C) was monitored *via* an YSI probe. HPLC-grade acetone from Aldrich was stored under Na₂SO₄ until use for all kinetic runs. Care needs to be taken to avoid advantageous water since the k_2 values will increase substantially depending on the amount of water present [6].

Product studies

The monoepoxides, **3a** and **3b**, were identified by GC-MS (Shimadzu GCMS-QP5000, Column: Supelco 2-4001 fused silica capillary SE-54 30 m length, 0.25 mm diameter) and ^1H NMR (Bruker-400 MHz) data. To 0.21 mmol of diene (**2a** or **2b**), 0.20 mmol of 0.088 M dimethyldioxirane in acetone was added at room temperature. After several minutes, GC-MS analysis showed that the monoepoxide was formed in excellent yield with slight amounts of unreacted diene present as well as traces amounts of diepoxides for each case. The acetone was carefully removed at 0°C under reduced pressure, yielding the monoepoxide in roughly 50% yield in each case. The ^1H NMR spectra were in good agreement with the published data [17].

3,4-Epoxyoctahydronaphthalene (3a): ^1H NMR (400 MHz, CDCl_3): δ 5.94 (m, 2H), 3.51 (m, 1H), 3.24 (m, 1H), 2.04 (m, 2H), 1.64 (m, 2H).

3,4-Epoxyoctahydro-2H-chromene (3b): ^1H NMR (400 MHz, CDCl_3): δ 5.77 (m, 1H), 5.60 (m, 1H), 3.46 (m, 1H), 3.12 (m, 1H), 2.07 (m, 2H), 1.3–1.8 (m, 6H).

Kinetics

Kinetic studies were carried out on a Shimadzu UV-3101 PC spectrometer with jacketed cells. A solution of dimethyldioxirane in dried acetone (known concentration) was placed in the jacketed sample cell and was allowed to thermally equilibrate at 23°C . The appropriate amount of cyclic diene stock solution in dried acetone was added rapidly and mixed (~ 4 s) *via* pipette. The disappearance of dimethyldioxirane was monitored vs. time at 330 nm for at least two half-lives. For 1,3-cyclooctadiene, pseudo-first-order conditions were employed with the diene concentration at least tenfold greater than that of **1**. For the more reactive 1,3-cyclohexadiene,

second-order conditions were employed. The k_2 values were the average of at least three experiments. All kinetic runs had correlation coefficients of 0.99 or greater. After completion of each kinetic run, formation of the monoepoxides was confirmed by GC-MS analysis.

Computational methodology

All calculations (gas phase) reported in this paper were performed with the Spartan'10 molecular modeling program. The DFT approach using Becke3-LYP and the 6-31 G basis set was utilized for all calculations. Energies for the minimized ground-state structures were determined for all the reactants [dimethyldioxirane (**1**), cyclic dienes (**2a** and **2b**), and the phenyl-substituted alkenes (**4a** and **4b**)] and the products [acetone, corresponding monoepoxides (**3a** and **3b**), and epoxides (**5a** and **5b**)]. As expected, the computational data predicted that the reactions are exothermic in all cases. The optimized ground-state energy structure of 1,3-cyclohexadiene was predicted to be a relatively flat *s-cis* system. The optimized ground state energy structure of 1,3-cyclooctadiene is consistent with the two double bonds not in the same plane with a torsion angle of 51°. The HOMO-LUMO energies were obtained from the optimized geometries using the DFT approach using Becke3-LYP and the 6-31 G basis set. As expected, the optimized transition state for each diene resulted in a spiro-orientation with a slight asynchronous tilt away from the other double bond of the cyclic system. Regardless of the initial approach of the dioxirane, all valid transition states resulted in the spiro-orientation. To save time, the calculations were carried out with the methyl groups of the dioxirane oriented away from the most hindered side of the diene, which always yielded the lowest energy spiro-transition state. Each transition-state calculation was checked for validity. A valid transition state had only one negative eigenvalue, which also corresponded to the eigenvector in a separate intrinsic reaction coordinate (IRC) calculation. When animated, the IRC linked the starting materials to the desired products through

the spiro-oriented transition state. For the cyclic dienes, two reaction sites are present and can be approached from the top or bottom, yielding different outcomes due to conformational factors.

Because 1,3-cyclohexadiene is relatively flat, the transition states for all approaches for monoepoxidation are of similar reactivity. Alternatively, for 1,3-cyclooctadiene, conformation is a major factor. All approaches to the reaction sites were calculated. Due to significant energy differences, one of the approaches was found to have a substantially lower electronic activation energy and therefore was the major contributor to the overall reactivity for that case. Weighted averages of the electronic activation energies for all orientations of attack of **1** on the other substrates were not necessary. For the other cases, the lowest electronic activation energy was taken as representative. As shown for simple *cis*-alkenes [5], the approach to *cis*-1-phenylpropene is with the methyl groups of the dioxirane away from the hindered side. For the *trans*-1-phenylpropene, the transition state with the lowest energy is with the methyl groups of the dioxirane oriented on the side of the phenyl substituent of the alkene rather than the side of the methyl group. Ground-state energy structures of the starting materials and the transition-state conformations were checked and corrected for conformational differences, if present. For **2b**, this was a problem that was solved by constraining the conformation of the starting material during the transition-state calculation. All calculations were completed in the gas phase at 23°C for this study. The electronic activation energies were calculated as follows: $E_{\text{elect}} = \text{energy of transition state} - (\text{ground-state energy of dioxirane} + \text{ground-state energy of substrate})$. To calculate the relative reactivities, the difference in the electronic activation energies was used (Arrhenius equation) in the following manner: $= (-E_{\text{elect}} / RT)$

$2\text{rel } 2k(e)(k \text{ normalized})$. The substrate with the lower reactivity is normalized to 1. Inclusion of a solvent in calculations, while affecting the individual values, did not affect the electronic

activation energy differences, in agreement with the literature [18]. Therefore, all calculations were completed in the gas phase at 23°C for this study.

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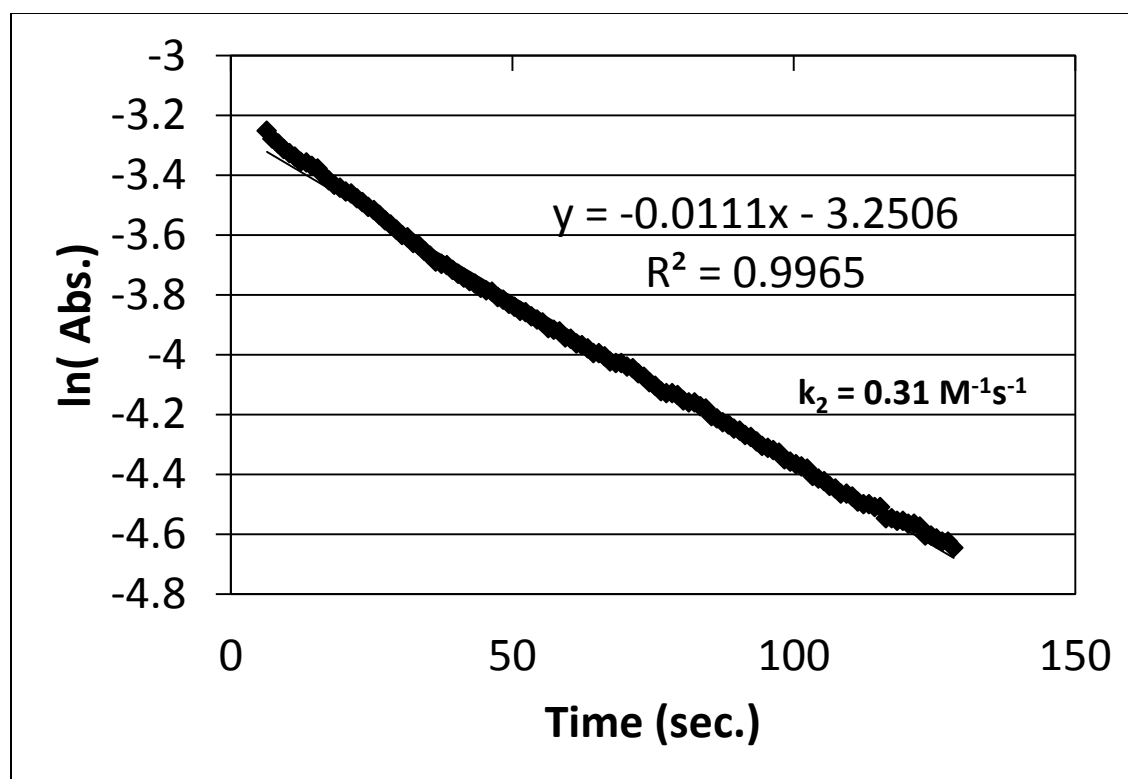
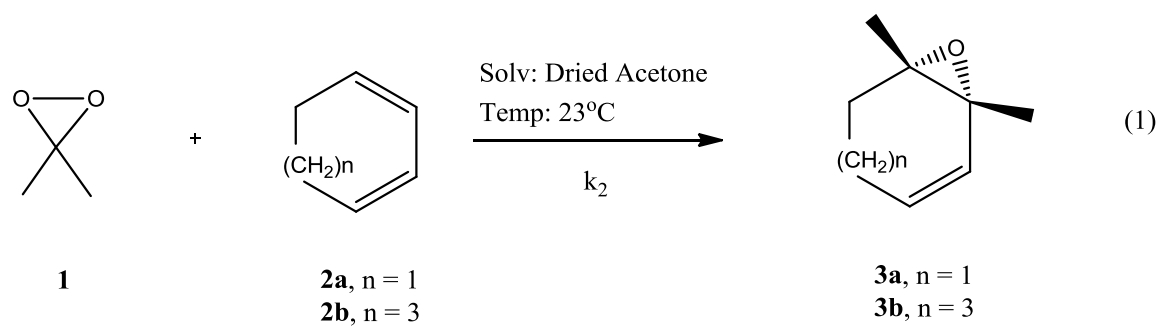


Figure 1. Representative pseudo first order plot for the monoepoxidation of 1,3-cyclooctadiene (**2b**) by **1** in acetone at 23°C.

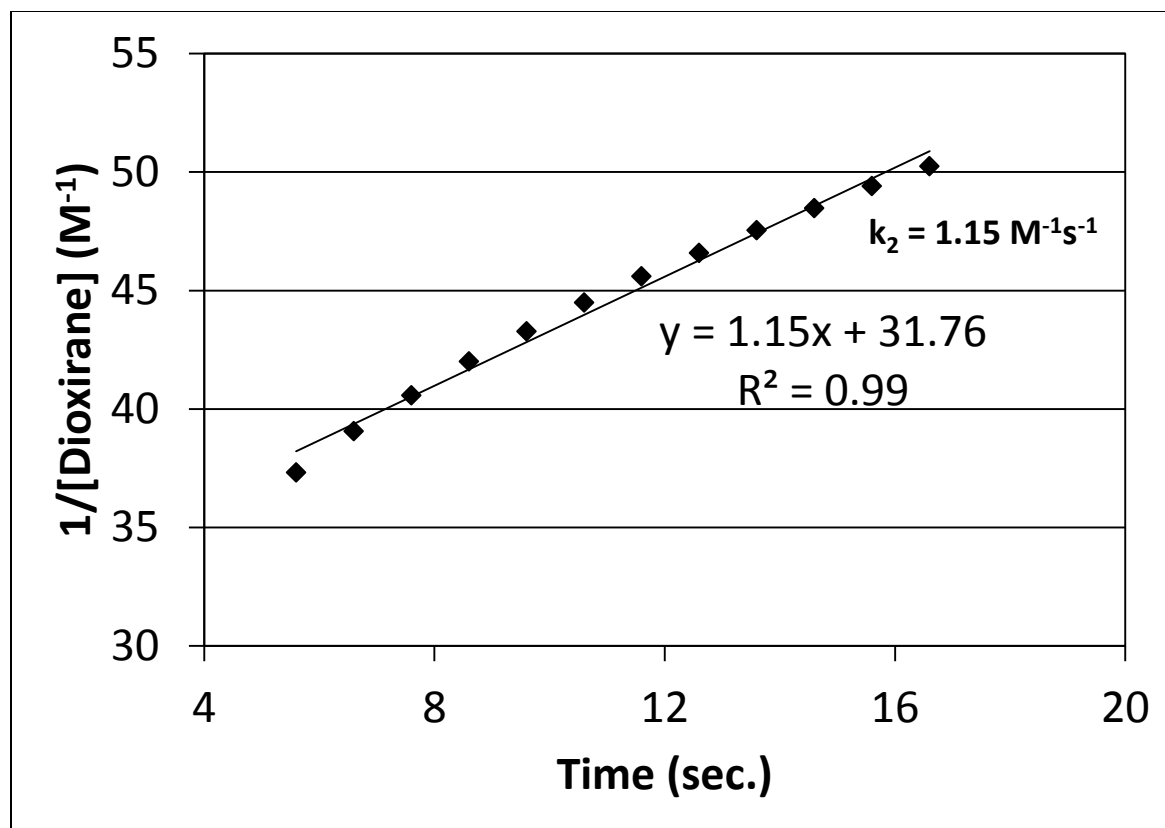


Figure 2. Representative second order plot for the monoepoxidation of 1,3-cyclohexadiene (**2a**) by **1** in acetone at 23°C.

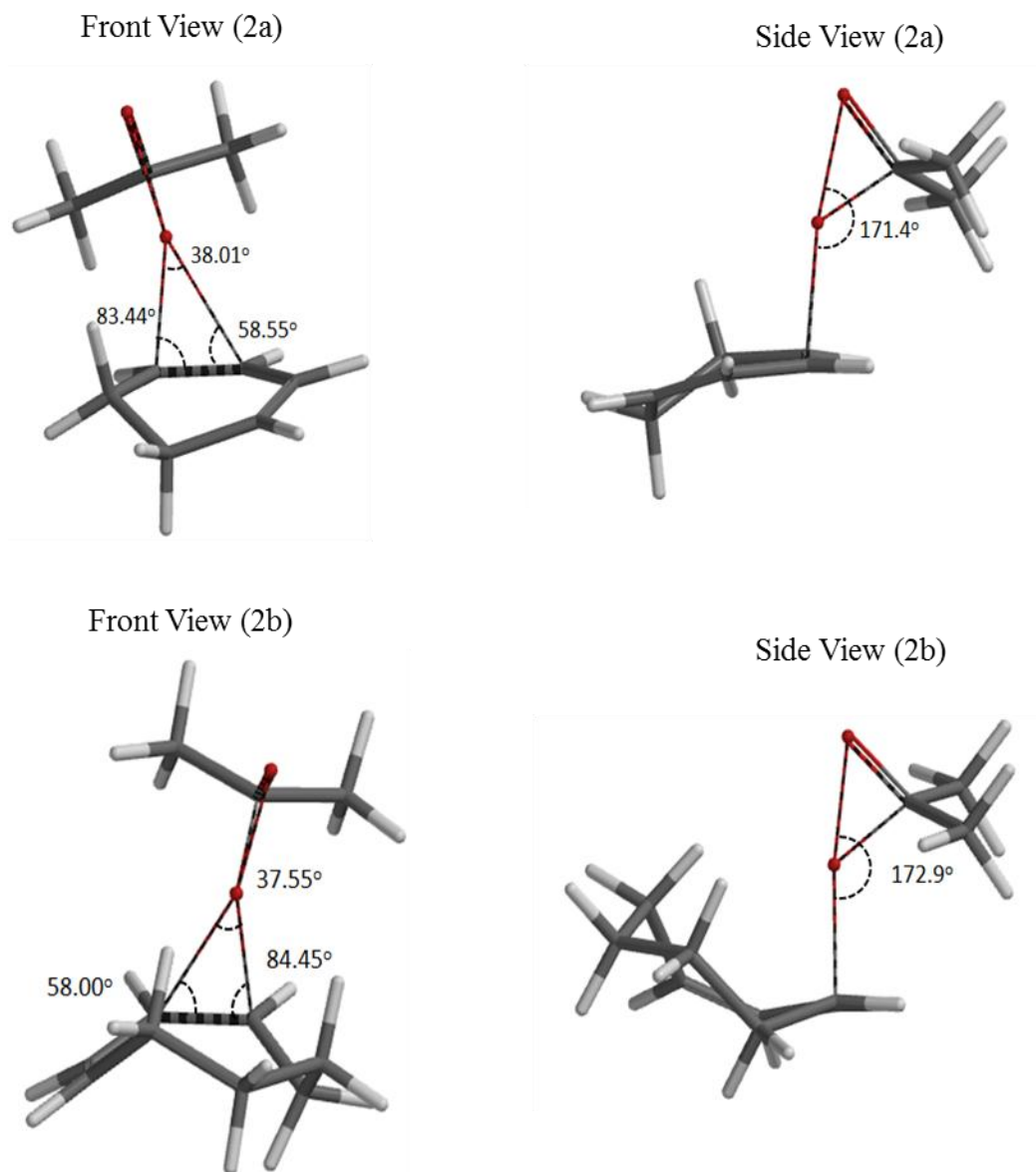
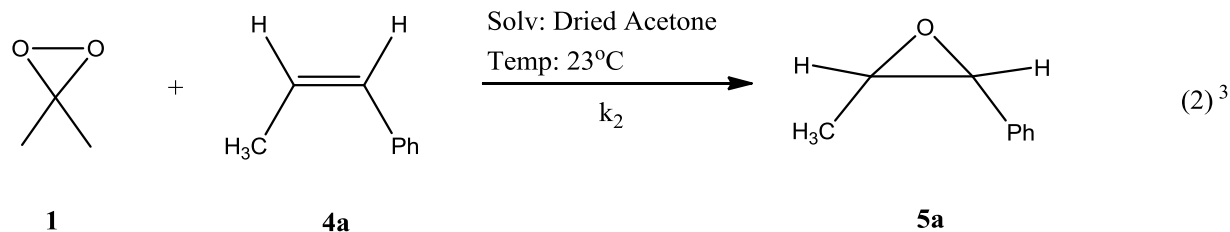


Figure 3. Calculated Density functional B3LYP 6-31G* transition state structures for the monoepoxidation of 1,3-cyclohexadiene (**2a**) and 1,3-cyclooctadiene (**2b**) by **1**.

Table 1. Experimental and predicted (DFT) data for the monoepoxidation of 1,3-cyclohexadiene (**2a**) and 1,3-cyclooctadiene (**2b**) by **1**.

Molecule	$k_{2\text{expt.}}$ ($\text{M}^{-1}\text{s}^{-1}$)	Total Ground state energies ^b (kcal/mol)	Transition state energy ^b (kcal/mol)	Activation energy ^b ($E_{\text{elect.}}$)	$\Delta E_{\text{elect.}}$	$k_{2\text{rel.}}$ (predicted)	$k_{2\text{rel.}}$ (experimental)
2a	1.14 ± 0.06	-314809.20	-314795.83	13.37	0.80	3.9 ± 0.3	3.7 ± 0.6
2b	0.31 ± 0.03	-364143.10	-364128.96	14.14		$\equiv 1^{\text{a}}$	$\equiv 1^{\text{a}}$

a) normalized b) calculated



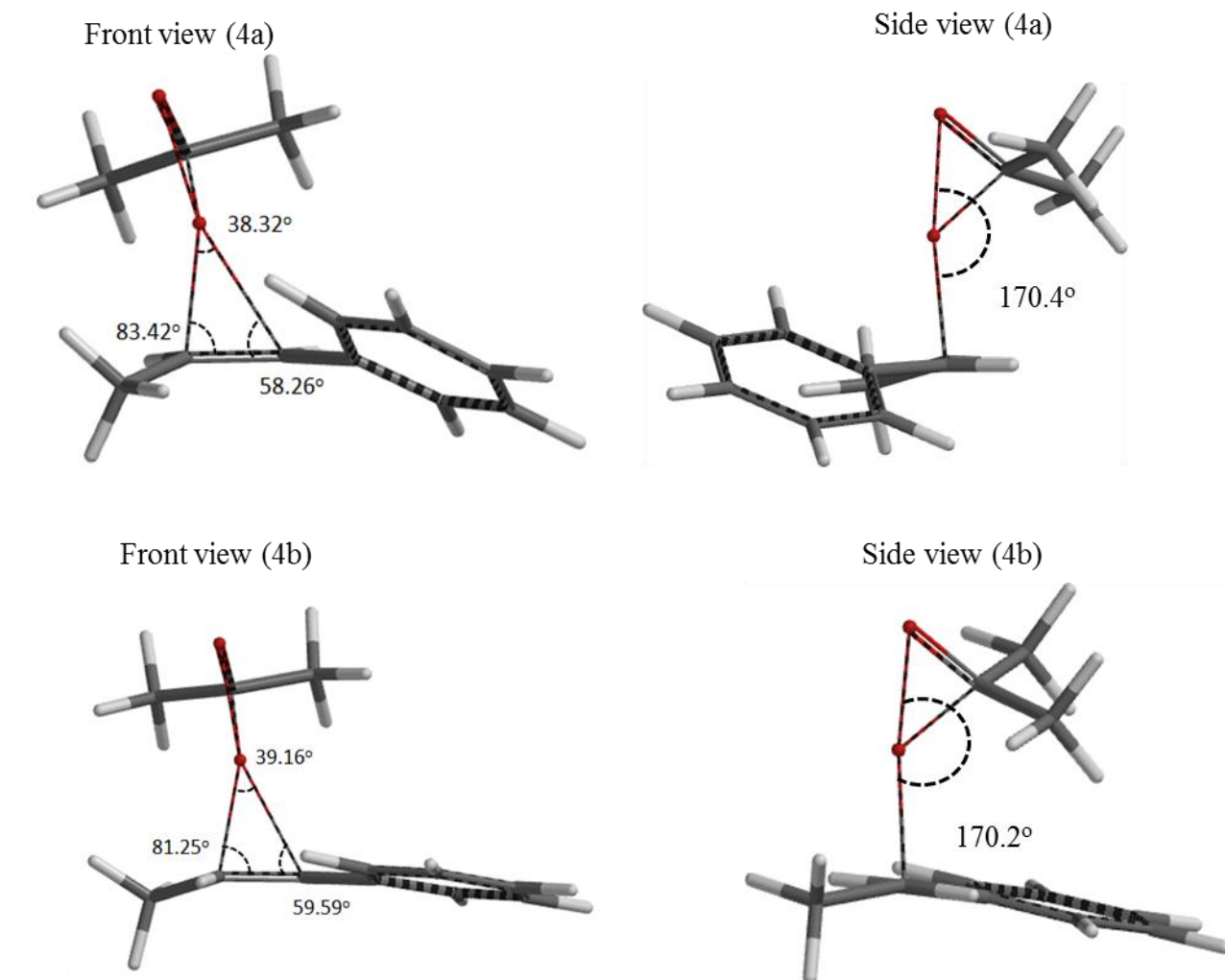


Figure 4. Calculated Density functional B3LYP 6-31G* transition state structures for the epoxidation of *cis*-1-phenylpropene (**4a**) and *trans*-1-phenylpropene (**4b**) by **1**.

Table 2. Experimental and predicted (DFT) data for the epoxidation of *cis*-1-phenylpropene (**4a**) and *trans*-1-phenylpropene (**4b**) by **1**.

Molecule	$k_{2\text{expt.}}$ ($\text{M}^{-1}\text{s}^{-1}$)	Total Ground state energies ^b (kcal/mol)	Transition state energy ^b (kcal/mol)	Activation energy ^b ($E_{\text{elect.}}$)	$\Delta E_{\text{elect.}}$	$k_{2\text{rel.}}$ (predicted)	$k_{2\text{rel.}}$ (experimental)
4a (<i>cis</i>)	0.18 ± 0.01	-387313.44	-387299.44	14.00	0.20	$\equiv 1^a$	$\equiv 1^a$
4b (<i>trans</i>)	0.29 ± 0.02	-387316.19	-387302.39	13.80		1.2 ± 0.2	1.6 ± 0.2

a) normalized b) calculated

Conclusions of the published study

- Kinetic studies found 1,3-cyclohexadiene to be around 4 folds more reactive than 1,3-cyclooctadiene towards monoepoxidation by dimethyldioxirane.
- 1,3-Cyclohexadiene has an overall reactivity similar to that of the monoepoxidation of acyclic conjugated dienes while 1,3-cyclooctadiene has an overall reactivity similar to that of the epoxidation of simple *cis*-alkenes.
- Basic DFT calculations predicted a spiro transition state geometry for the monoepoxidation of both cyclic dienes and predicted relative reactivity comparable to experimental relative reactivities.
- Application of the DFT approach for the epoxidation of *cis*-/ *trans*-1-phenylpropene successfully predicted the unexpected reactivity of the alkene pair with the *trans*-alkene being more reactive towards DMDO epoxidation than the *cis* isomer.

- This basic DFT method is a reliable approach for detecting the relative reactivity of dimethyldioxirane epoxidation.

CHAPTER TWO: ADDRESSING MISCONCEPTIONS ABOUT ENERGY CHANGES IN CHEMICAL REACTIONS THROUGH HANDS-ON ACTIVITIES

2.1 Introduction

The lack of interest towards science held by many middle and high school students in the United States has contributed to the health and economic crisis in the United States.¹ Education in the science, technology, engineering, and mathematics (STEM) fields has become a rising concern within the business and academic populations.² The threat exists that not enough Americans know enough about science and math to successfully compete ,or contribute to the growing knowledge-based civilization that is shaping our world. Furthermore, parents are not equipped with enough basic STEM knowledge or understanding of its importance to encourage their children to study these subjects. Other countries, learning from our history, have started to invest in the science and engineering disciplines. They realize that the effect that this investment in STEM yields increasing economic and social dividends.^{1,2} The growing competitive workforce in the science and engineering fields from other nations (Figure 16) is forcing the United States to address the apathetic attitude towards science by American students and determine whether our educational system is providing the skills to meet the demands of this century.²

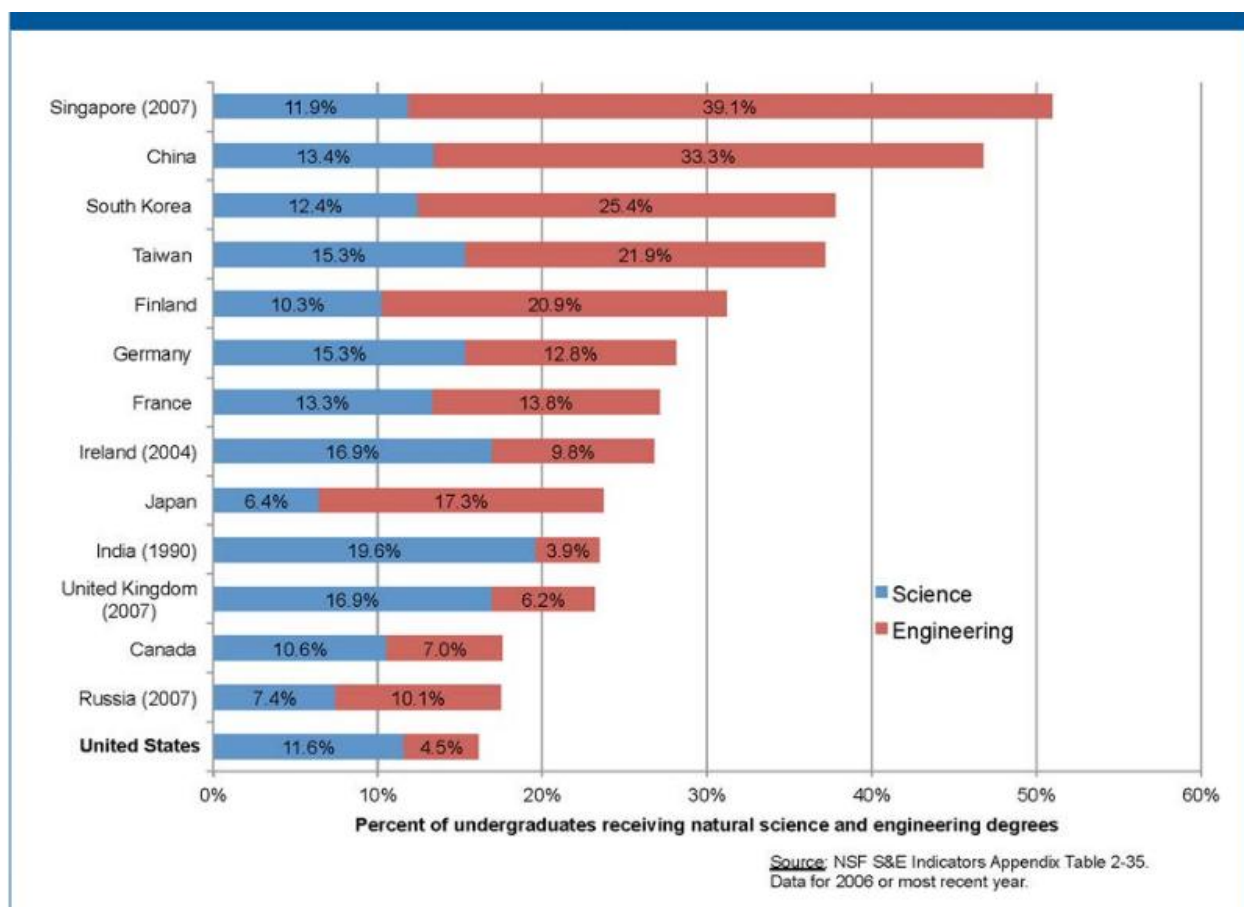


Figure 16. Percentages of undergraduates receiving degrees in the natural sciences and engineering in selected nations.^{2b}

2.1.1 National Educational Challenges

There are many challenges that our nation is facing to improve the quality of our students and their preparation to be able to contribute to the advancement of science and ultimately the nation. Some of the challenges include topics such as K-12 student performance in the science and mathematics disciplines, the lack of interests in undergraduates wanting to major in science and engineering, and attrition of our undergraduate and graduate students working towards science and engineering degrees.

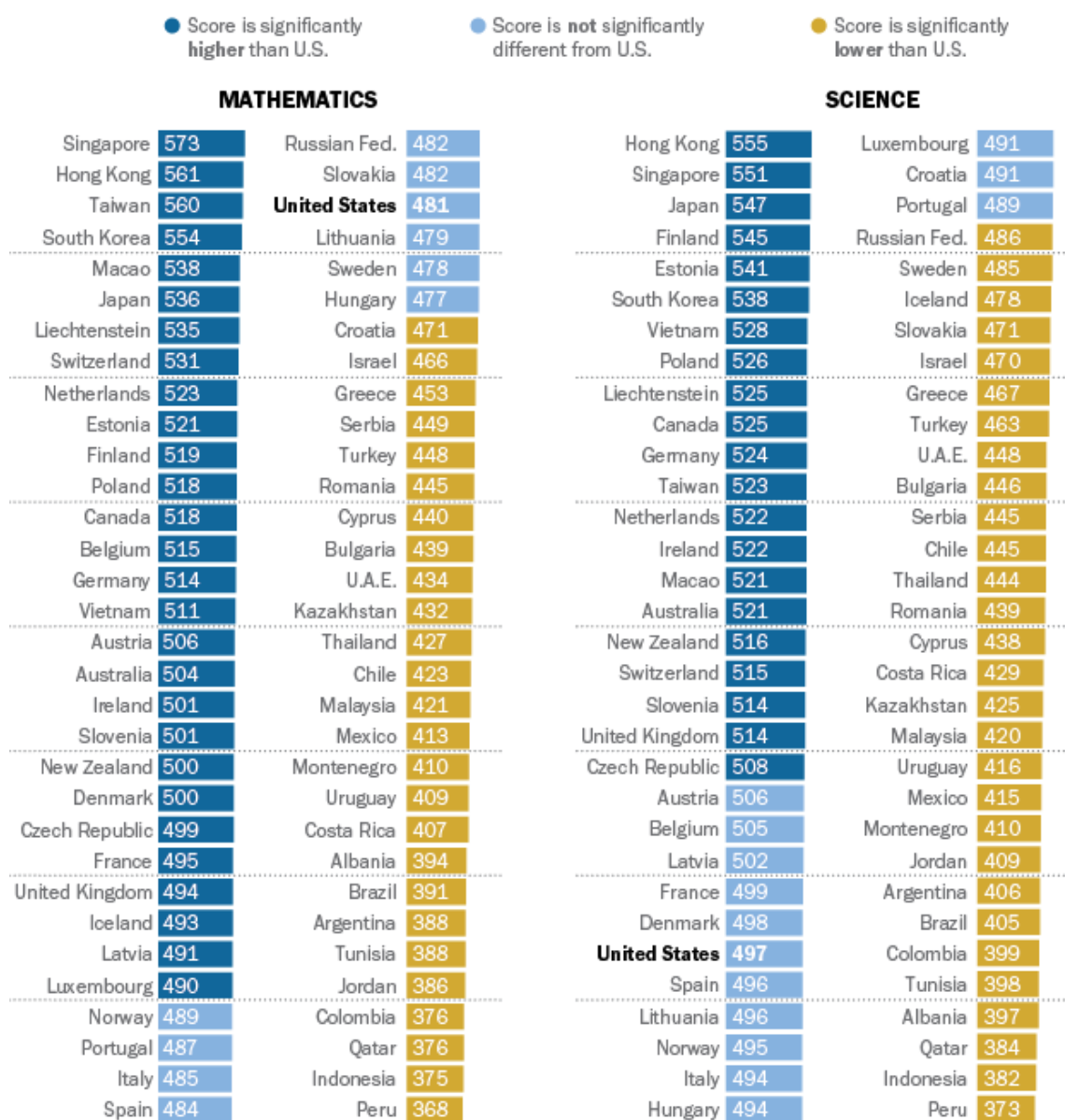
The latest IMD International World Book ranks the United States as number one in economic competitiveness followed by Switzerland, Singapore, and Hong Kong.³ The survey measures economic performance, governmental proficiency, business proficiency, and infrastructure. The Organization for Economic Co-operation and Development (OECD) states that the United States leadership in science and engineering has led to its economic advantages and quality of life.⁴

Student performance evaluations amongst US students are inconsistent with the US's economic competitiveness compared to other nations. Though US students are scoring higher on national science and math assessments, our nation still remains in the middle ranking compared to other nations (Figure 17). Members of the American Association for the Advancement of Science stated that the US STEM education is the best or above average, while 46% stated that US K-12 STEM education is below average.^{4b}

Another major educational challenge in the US educational system is the under-representation amongst women and minorities. White American males comprise of nearly 70% of the science and engineering workforce but just 40% of the overall workforce, while white American females make up about 35% of the overall workforce and around 15% of the science and engineering workforce.⁵ There are even more alarming statistics when race is taken into account. African Americans, Hispanics, and Native Americans make up 24% of the population but only 7% of the science and engineering workforce. White students scored higher than black and Hispanic students across all three grades (4, 8, and 12) in the 2009 science assessment comprised from data provided by the US Department of Education (Figure 18).^{4c}

Internationally, U.S. Stands in Middle of Pack on Science, Math Scores

Average scores of 15-year-olds taking the 2012 Program for International Student Assessment



Note: Scale ranges from 0-1,000. Results for China are not shown because only Shanghai fully participated in PISA 2012.
Source: OECD, PISA 2012 via National Center for Education Statistics

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Figure 17. Average scores of 15 year olds taking the 2012 Program for International Student Assessment.

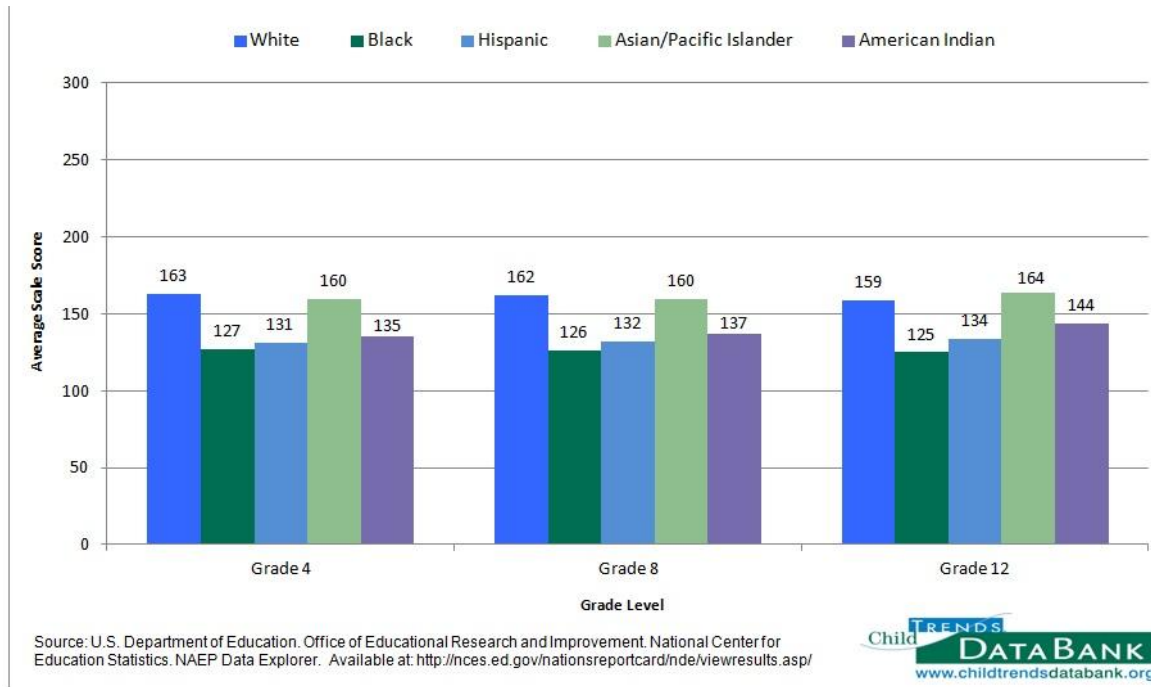


Figure 18. National science scores amongst students in grades 4, 8, and 12 by race/hispanic origin (2009).

Combined, minorities and women makes up more than half of the US population, and thus will make up the nation's new majority. If we were to provide the resources to strengthen the knowledge of this group in the STEM fields our talent pool will increase so that our growing demands of science and technology will be met.

As the 1960s and 1970s generation begins to retire, our colleges and universities are not producing enough scientists, engineers, and mathematicians to fill positions towards the advancement of novel technologies. We have become accustomed to the advancement of sciences that have been developed from the previous generation such as the World Wide Web, electronic mobile devices, and email. The items that we take for granted such as the energy-saving appliances in our homes, medical aid in emergencies, vast organization of electrical power, sanitation, and safe drinking water would not be possible without the advancement of

science, math, and engineering. We have to address this quiet crisis before we begin to experience the wrath of our nation's unpreparedness towards student development of the science, technology, engineering, and mathematics field.

2.1.2 State of Georgia Educational Performance, Needs, and Assessment

The Georgia CRCT is a standardized test that measures a student's proficiency in a core subject such as reading, math, science, and social studies.⁵ The CRCT is given to Georgia students grades 3-8. The percentage of the students who are meeting or exceeding expectations has increased from 2009 to 2013 as displayed in Figure 19.^{5a} There was an 86% math efficiency in 2013 and 79% met or exceeded expectations in science. Though the scores seem very promising, the provided assessment shows an inflated picture of the number of students proficient in these subjects. A recent *Education Next* article revealed that Georgia has the lowest ranking for the strength of state proficiency standards than any other state in the nation for math and reading. The authors, Harvard professor Peter Peterson and student Peter Kaplan, rated each state on a scale from A-F based on the alignment of proficiency rates on state assessments and the National Assessment of Educational Progress (NAEP). NAEP is a biannual assessment of given to a sample of 4th and 8th grade students in each state. Georgia received an "F" and ranked last among the 50 states and District of Colombia, which means Georgia sets low expectations for proficiency on the CRCT (Figure 20).

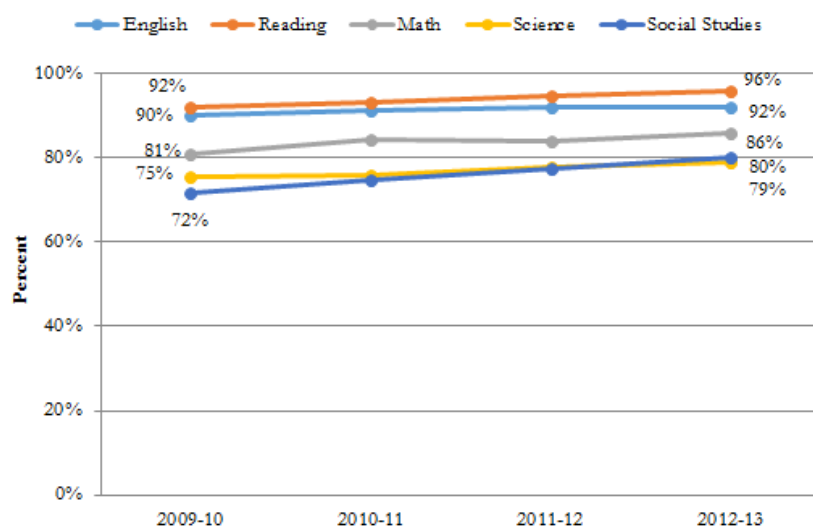


Figure 19. CRCT Percent Meet/Exceeds.

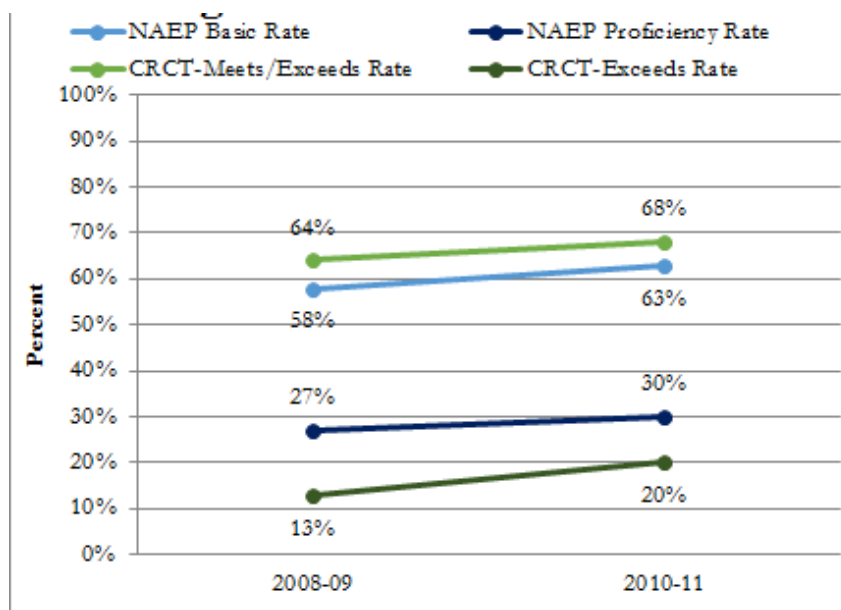


Figure 20. Eighth Grade Science Proficiency Rates CRCT/NAEP.

Georgia's K-12 performance on preparation of college, college participation, and college graduation rate continues to lag behind the national average, though there has been a modest improvement over the last decade.⁶ The average graduation rate for Georgia is 67% while the national average graduation rate is 76%. The likelihood that a ninth grader will attend college

right after high school increased from 31% in 1998 to 41% but still falls under the national average of 44%. In 2002, approximately 47% of Georgia's first-time full-time college students completed a bachelor's degree within six years which is lagging behind the national average (56%) and top states average (65%).

By 2018, 58% of Georgia jobs are projected to require a postsecondary degree or training.⁷ Unfortunately, Georgia ranks 29th amongst states with persons 25 and older with at least an associate's degree at 34%. Georgia's college age population (age 18 to 24) is projected to increase by 40, which is a burden for the state's K-12 and higher education institutions.⁶ One way to address this burden is for colleges and universities to step-up and provides the desperate assistance needed to help improve the Georgia student at an early stage.

Georgia State University is an urban research university located in the heart of downtown Atlanta. Because of its thriving science research component GSU's science professors place a great interest on recruiting students with a zeal for science inquiry. GSU science departments have also observed that there is a direct correlation between students' interest to learn more about science and students' pre-college exposure to inquiry-based science. Members of the Georgia State University community are willing to provide any assistance to help K-12 teachers give their students an authentic and engaging science experience. As a result, these efforts will produce more incoming students with an appreciation for science exploration.

2.1.3 Misconceptions in Chemical reactions, Energy, and Exothermic/Endothermic

In the early 1990s Fensham stated that "The most conspicuous psychological influence on curriculum thinking in science since 1980 has been the constructivist view of learning."^{9a} Constructivism states that students build new knowledge based on their pre-existing knowledge. However, research shows that teachers have issues incorporating student's pre-existing

knowledge in their courses because of common misconceptions that have never been addressed.^{9b-9c} Since pre-existing knowledge in science is important in acquiring new knowledge, several studies have been carried out covering topics such as chemical reactions, chemical equilibrium, bonding, and thermodynamics.¹⁰ In the case of thermodynamics, studies revealed that students have trouble in comprehending and differentiating between endothermic and exothermic reactions. Other misconceptions concerning thermodynamics have been uncovered. For example, Ross observed students' belief that energy is released when chemical bonds break.^{10a} Ross believes this misconception was developed by students who associate fuel with energy. This association develops further into the reasoning that fuel is an energy store in chemical bonds, therefore once those bonds are broken energy is released. Another study involved asking twenty 15 year olds about the topic of conservation of energy. Two-thirds of the students said that the "energy was used up or lost."^{10b} Ross believes that this misconception is created by students because of everyday experiences such as a battery going dead and having to recharge it for use or having to refuel the tank of a car because the gas was "used up." Other common thermodynamic misconceptions include students' belief that endothermic reactions occur spontaneously and the belief that energy is created in chemical reactions.^{10c} Students also have difficulties in differentiating between enthalpy change and activation energy.^{10d} The "Hot or Cold Does it Matter" module was created to address the following misconceptions: heat is always needed to start a chemical reaction; all chemical reactions create or destroy energy; the atoms of the reactants in a chemical reaction transforms into other atoms once the reaction occurs; after a chemical reaction occurs the product is a mixture where the old substances persist and no new compounds are produced; and burning a candle is an endothermic reaction since heat is absorbed to initiate the reaction. These misconceptions will be addressed by providing visual

aids, demonstrations, and hands-on experiments in order to further engage students and improving students' interest in science.

2.1.4 Module Design and Goals of the Study

The development of the discussed module entitled “Hot or Cold, Does it Matter” was established to address misconceptions concerning the topics of energy influences in chemical reactions. The funding for the development of the module was provided by the U.S. Department of Education GAANN Fellowship and the Bio-bus program. The Bio-bus program, under the direction of Dr. Barbara Baumstark, is a NSF and NIH funded program at Georgia State University that was created to share the excitement of science to the Georgia community. The Bio-bus is a 30-foot mobile instructional laboratory that travels to K-12 schools free of charge and presents engaging hands-on activities and demonstrations covering many science disciplines including geoscience, microbiology, biology (DNA), biotechnology and forensics, and chemistry. The Bio-bus program has made over 2,500 visits to participating schools and community organizations located in 31 different Georgia counties since its inception in 1999. The Bio-bus is an exceptional outreach program that makes science assessable to all Georgians by bringing the laboratory to students to resolve that “inquisitive enigma” of science, by integrating scientific investigations into the classroom, and by providing engaging hands-on experiments that mirrors actual practices carried out by many professional scientists. The ultimate goal of the module development and study was to expose Georgia grade 8-12 students about energy influences in chemistry and to address the common misconceptions regarding the topic of energy.

The module implemented several Georgia Performance standards for 8th-12th grades which includes the Characteristics of Science (CS) standards along with content standards for

physical sciences (P). The module covered content knowledge that was not limited to one grade level so the project could easily be taught to a variety of grade levels and could provide a diverse learning experience covering several standards.

Overall, students were able to explore the curiosity, honesty, openness, and skepticism in science (S8CS1 and SCSH1). Students were able to use standard safety practices for classroom laboratories (S8CS2 and SCSH2). Students were able to communicate scientific investigations and information clearly (SCSH6). Students were able to use tools and instruments for observing, measuring, and manipulating equipment and materials in scientific activities (S8CS4 and SCSH4). Students were able to examine the scientific nature of matter (S8P1) its classifications, and its system of naming types of matter (SPS2). Students were able to familiarize themselves with the forms and transformations of energy (S8P2). Students were able to relate transformations and flow of energy within a system (SPS7).

2.2 Methodology

2.2.1 Participants

Students involved in this study attended high schools in underrepresented areas that lacked the usual options provided for science courses. For example, both schools had removed advance and AP chemistry courses from their curriculum. A total of two visits served 106 students. The race/ethnicity of each student was as follows: Black (50 students), Hispanic (36 students), White (4 students), Asian (4 students), and other (3 students). The grade levels of each student were as follows: 10th (25 students), 11th (54 students), and 12th (7 students). The genders of each student were as follows: female (36 students) and male (57 students). The class consisted of students taking either physical science or general chemistry. None of the students were introduced to the topics of endothermic or exothermic reactions prior to the module. Students

taking chemistry courses had general knowledge of chemistry. For example, students' were able to define matter and atoms, and the relay characteristics of the periodic table.

2.2.2 Module Design Components

Demonstrations were incorporated into the module so that the students were able to interpret the information through visual aids. The first demonstration was the luminol experiment. This demonstration was carried out in the beginning of the module to grasp the attention of the students. The luminol experiment demonstrated an exothermic reaction which released light as a form of energy (Figure 21). The following demonstration, the chameleon experiment, demonstrated how color change can determine if a chemical reaction has taken place. This experiment changes four different colors within 30 seconds and really delivered the observation of color changes in a chemical reaction. The next two demonstrations described factors that can control the rate of a chemical reaction. Glow sticks were broken and placed in a beaker of boiling water and another in a beaker of ice water (Figure 22). The students were able to observe how the glow stick in the boiling water was illuminating brighter than the glow stick in the ice water. The other demonstration was the elephant toothpaste which used a catalyst (potassium iodide) to speed up the decomposition of hydrogen peroxide. Students were able to observe the hydrogen and oxygen gas being released as well as heat coming off of the exothermic reaction.



Figure 21. Luminol experiment demonstration shown in "Hot or Cold, Does it Matter?" module.



Figure 22. Glow sticks demonstration shown in "Hot or Cold, Does it Matter?" module.

Hands-on experiments were also incorporated. The first two hands-on experiments demonstrated physical and chemical changes with an Ivory® soap experiment and a penny experiment. Ivory soap has tiny air pockets incorporated into its design. When microwaved the soap begins to expand. Students were able to wash their hands after the soap was microwaved and saw that the soap has the same properties as before being microwaved and only a physical change had taken place. The next two hands-on experiments incorporated the ideas of exothermic and endothermic reactions. The endothermic experiment is the reaction of citric acid with sodium bicarbonate. First, students were instructed to record the initial temperature of the citric acid solution. The students were then asked to add the sodium bicarbonate and record the temperature at different time points. Overall, students observed that the temperature decreased approximately seven degrees. The exothermic experiment observed the decomposition of 6% hydrogen peroxide catalyzed by yeast. Students were instructed to record the initial temperature of the 6% H_2O_2 and then add the yeast and record the temperature at different time checkpoints. Overall, students observed an approximate thirty degree increase in temperature. The handouts given to the students for all four hands-on experiments are displayed in Appendix A.2.1 and A.2.2.

Common misconceptions on energy influences were also addressed in the PowerPoint presentation. The PowerPoint presentation consisted of 16 slides as displayed in Appendices A.2.4-A.2.21. The presentation provided a visual aid including animations to attempt to give a clear explanation of the covered topics. For example, to explain the differences in the amount of energy absorbed and released in endothermic and exothermic reactions slides 12 and 14 in Appendices A.2.16 and A.2.19 respectively, displayed animations. The animation for the endothermic reaction displays a big arrow of energy being absorbed to break the bonds and a

smaller arrow of energy being released when the new bonds are formed. The animation for the exothermic reaction displays the exact opposite, by showing small arrows of energy being absorbed to break the bonds of an exothermic reaction and larger arrows of energy being released after the new bonds are formed.

2.2.3 Surveys and Data Analysis

Surveys were implemented to provide objective feedback for both process and outcomes of the module (Appendix A.2.3). Students' attitude towards science and content of knowledge was taken before and immediately after the module as well as one month later. Students' attitude towards science was evaluated by using a Likert scale agree/disagree survey (1 = strongly disagree, 2 = disagree, 3 = in between, 4 = agree, 5 = strongly agree). This portion of the survey included statements reflecting the student's interest, perception of science, and their confidence levels in science (Table 14). Another portion of the survey included content knowledge questions about different chemistry topics such as matter, changes in matter, energy, what governs a chemical reaction, and endothermic/exothermic reactions (Table 15). The survey also included demographic questions such as race/ethnicity, grade level, and gender. A question that asked the student to draw their depiction of a scientist was also included to help further determine the student's perception of a scientist. Both pre- and post-surveys were administered by Bio-bus personnel and taken for analysis.

Table 14. Student attitudinal question on pre- and post-surveys.

Question #	
1	I like science.
2	I am good at science.
3	Science is interesting.
4	I think I could be a scientist.
5	I feel I can understand science.
6	I would like to learn more about science.
7	Science is one of my favorite subjects.
8	To become a scientist I have to have a good memory.

Table 15. Concept knowledge questions on pre- and post-surveys.

Question #	
9	What is ALWAYS needed for a chemical reaction to occur?
10	Which of the following statement is true about the role of energy in all chemical reactions?
11	Which of the following could represent a chemical reaction?
12	Burning a candle is an endothermic reaction since heat is absorbed to initiate the reaction. True/False
13	Energy is released to the environment which reflects why exothermic reactions feel warm.

2.3 Results and Discussion

Results obtained from the assessment of the surveys provided a way to measure the student's progression in content knowledge and attitude towards science. The pre-surveys were administered immediately before the module began. The post-presentation surveys were administered the same day immediately after the conclusion of the module and then one month later. SPSS analysis software program was utilized to analyze all data.^{13a} An Exploratory Factor Analysis (EFA) was used to convey the underlying structure of the attitudinal questions and to gain knowledge on how the items relate to each other. The results of the EFA revealed the presence of two factors 1) "Student's Interest in Science" and 2) "Student's Science Self-Efficacy" as described in Table 16. Cronbach's alpha (α) is a measurement that determines the internal consistency of a factor.¹³ That is, it describes how well a set of items on a test or survey measure a particular construct or a particular characteristics of individuals. The closer Cronbach's alpha coefficient is to 1.0 the greater the internal consistency of the items in the scale. An alpha score of 0.80 or higher constitutes to a very good reliability measurement ; an alpha of 0.65 is considered acceptable. Cronbach alpha measurements determined for the "science interest" and "science self-efficacy" was 0.89 and 0.79, respectively. These values are considered very good reliability for both factors (Table 16). It was also observed that if any of the items were deleted

from each construct that the Cronbach alpha value will be decreased. Table 16 includes the Cronbach value that resulted if the item was deleted.

Table 16. Exploratory Factor Analysis and Cronbach Alpha Measurements.

	Factors	
	Science Interest ($\alpha = .89$)	Science Self-Efficacy ($\alpha = .79$)
1. I like science.	$\alpha = .84$	
3. Science is interesting.	$\alpha = .88$	
6. I would like to learn more about science.	$\alpha = .87$	
7. Science is one of my favorite subjects.	$\alpha = .85$	
2. I am good at science.		$\alpha = .65$
4. I think I could be a scientist.		$\alpha = .75$
5. I feel I can understand science.		$\alpha = .78$

Student interest and science engagement was measured by the use of a Likert scale agreement to the following questions, “I like science”, “Science is interesting”, “I would like to learn more about science”, “Science is one of my favorite subjects.” Independent sample t-tests were carried out to determine if the data provided any significance between the pre- and post-survey. Results that show a significant difference between pre- and post-surveys have values of $p < 0.05$. Immediately following the conclusion of the module students showed a significant increase ($p < 0.05$) in liking science and wanting to learn more about science and a significant increase ($p < 0.05$) in response to science being one of their favorite subjects (Figure 23). For the items concerning students’ science self-efficacy students’ show a significant increase ($p < 0.05$) in “I think I can be a scientist” and a significant increase ($p < 0.05$) in “I am good at science.” Overall, students showed a significant increase in 5 out of the 8 attitudinal questions (Figure 23) from responses for surveys completed immediately following the conclusion of the module.

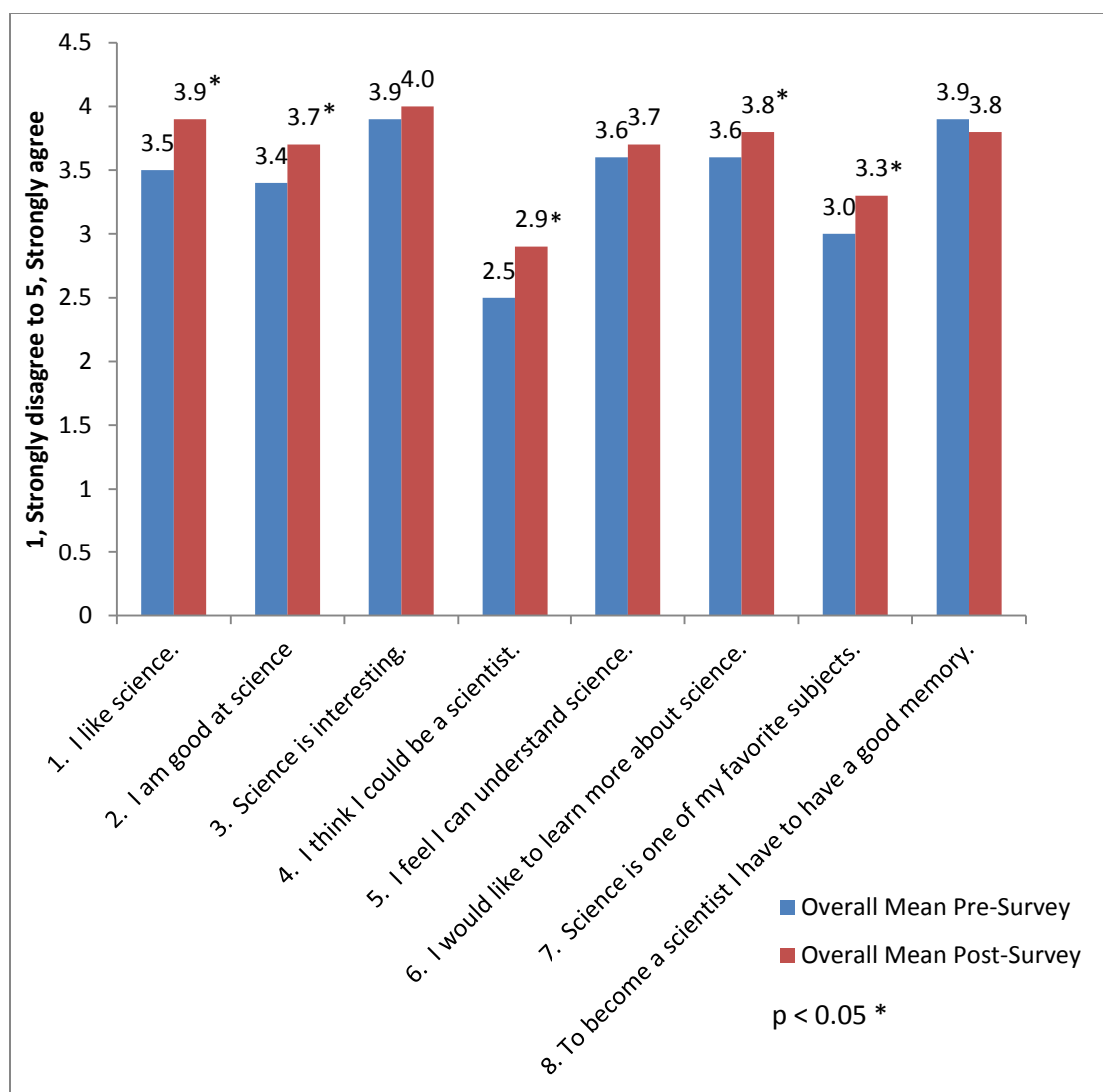


Figure 23. Overall attitudinal results.

Gender-based attitudinal results revealed that females (Figure 24) showed a significant decrease ($p = 0.03$) in the question, “To become a scientist I have to have a good memory,” while males (Figure 25) did not display any significant difference in the pre and post data for attitudinal questions. Overall, the students show an increase in science interest and science confidence after participating in the study which can help explain why it is important to provide students with hands-on experiences to further develop their interest in science. Significance was

more than likely not detected for the gender-based data due to the smaller sample size from dividing the sample group into two smaller gender-based groups.

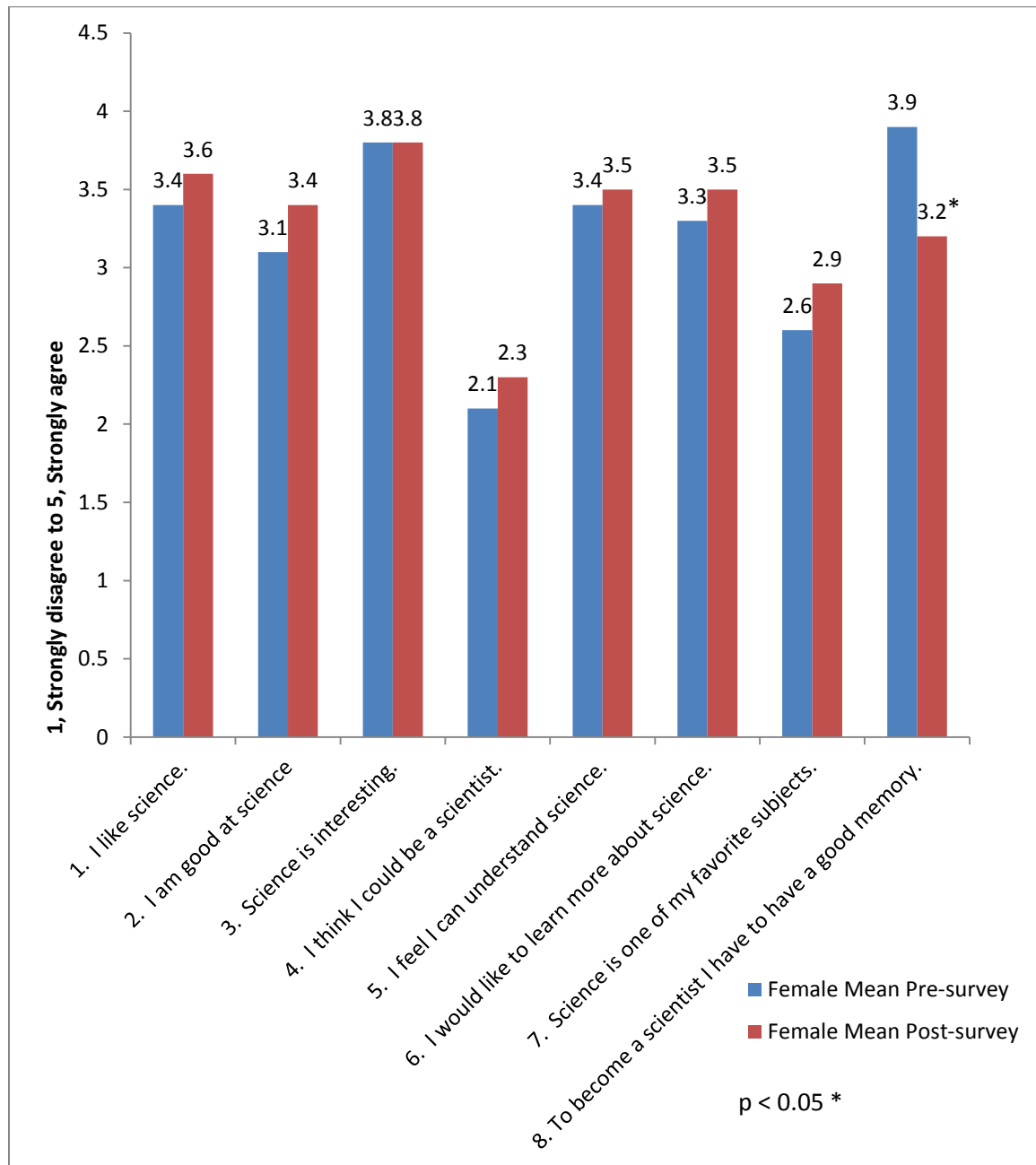


Figure 24. Female attitudinal results.

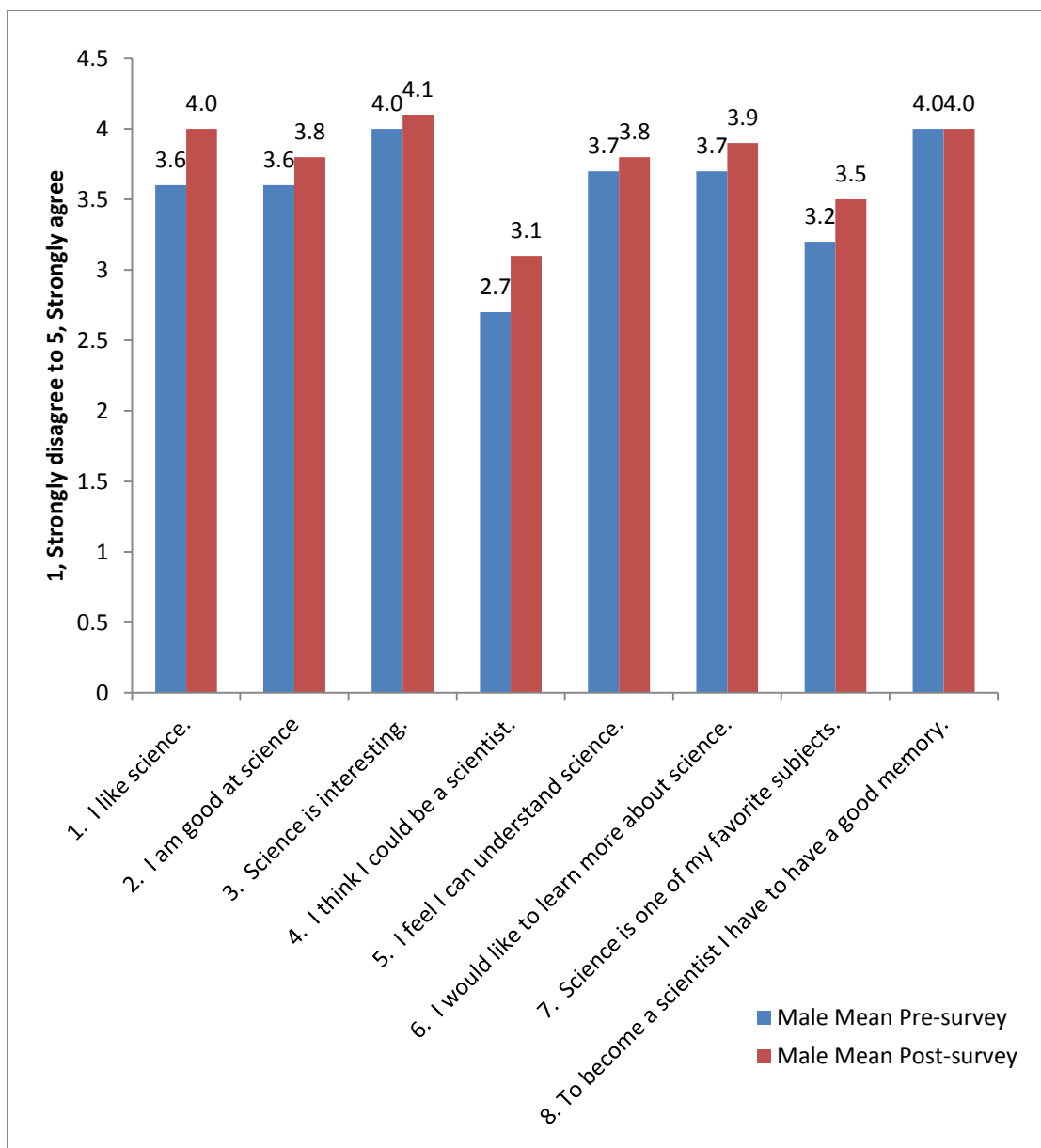


Figure 25. Male attitudinal results.

Content knowledge results showed that there is a significant increase in two of five content knowledge questions including Question 11, Which of the following could represent a chemical reaction? ($p < 0.05$) and Question 12, Burning a candle is an endothermic reaction since heat is absorbed to initiate the reaction., ($p < 0.05$) as shown in Figure 26. Gender-based

content knowledge questions results also showed a significant increase in Question 11, Which of the following could represent a chemical reaction? ($p < 0.05$) for male participants (Figure 28) and Question 12, Burning a candle is an endothermic reaction since heat is absorbed to initiate the reaction., ($p < 0.05$) for female participants (Figure 27). It is important to note that all post-surveys showed an increase in content knowledge with the exception of the content knowledge Question 10 for female participants that showed a slight decrease as shown in Figure 27.

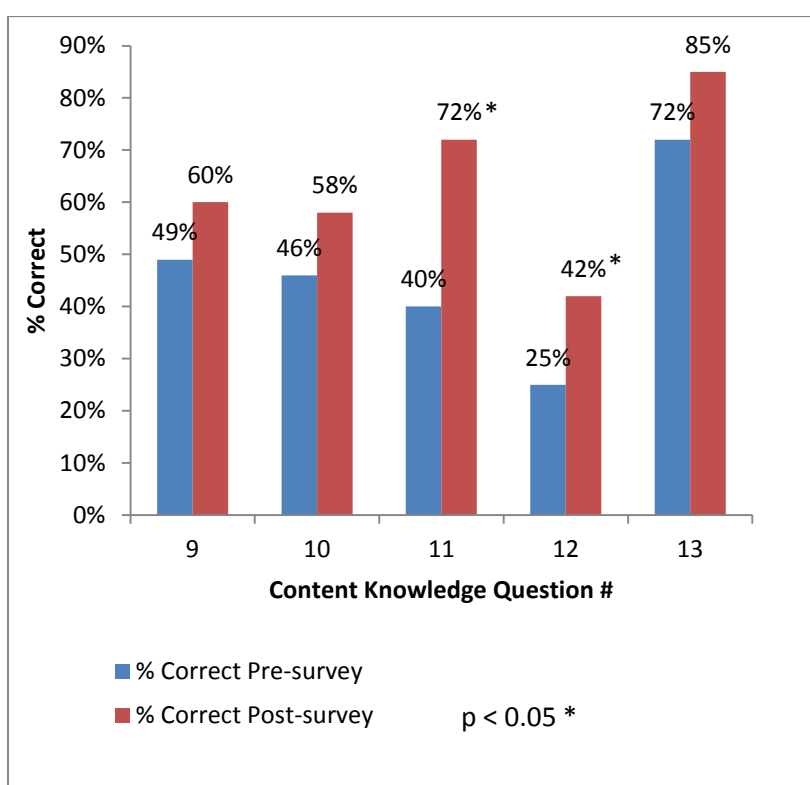


Figure 26. Overall content knowledge results.

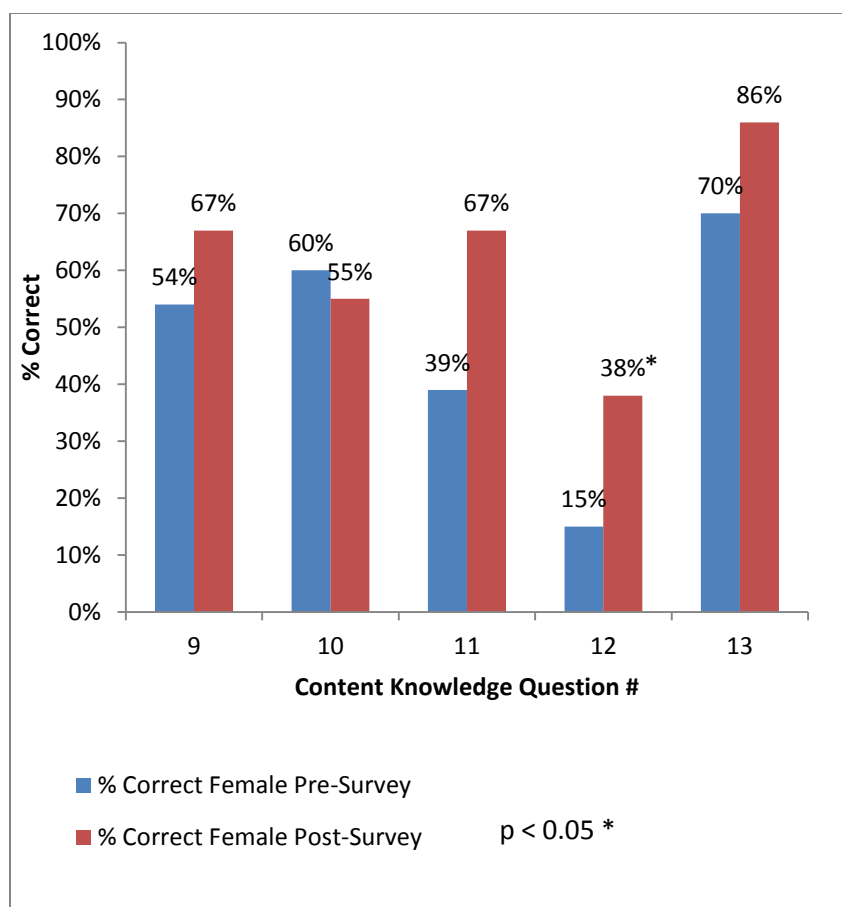


Figure 27. Female content knowledge results.

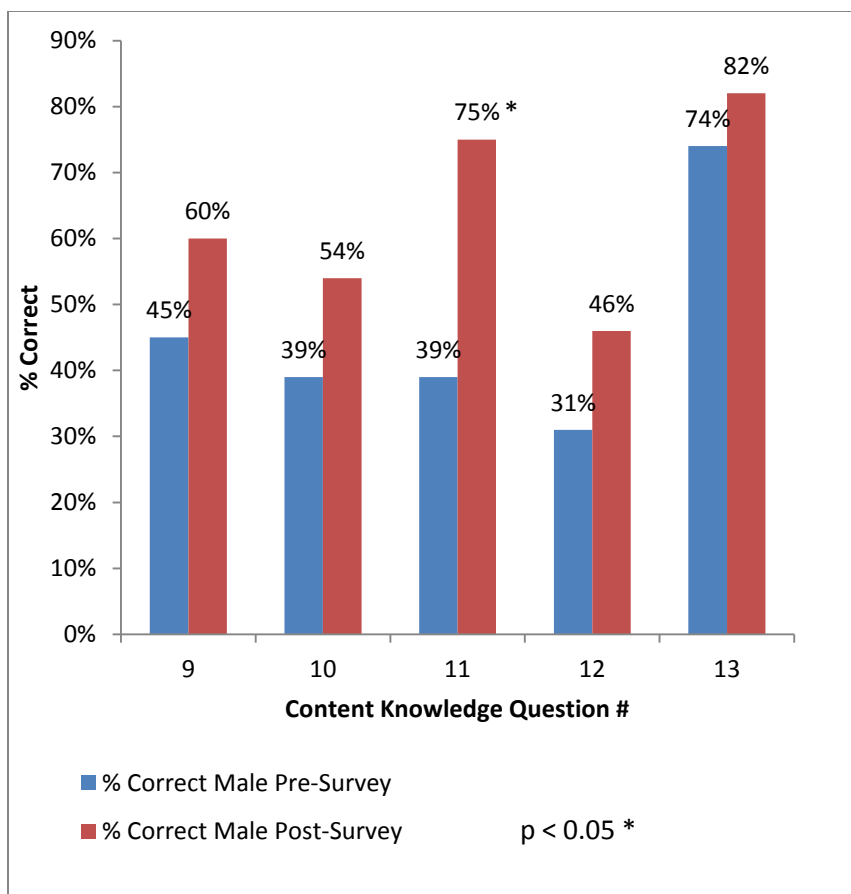


Figure 28. Male content knowledge results.

The learned concept for Question 11 is that when compounds interact to make new compounds, the atoms that make up the molecules of the original compounds rearrange into new molecules. The misconceptions that are associated with this concept is that students often believe that the atoms of the reactants transforms into other atoms¹¹ answer choice A or after a chemical reaction occurs the product is a mixture where the old substances persist and no new compounds are generated¹² answer choice C. The paired t-test results showed that there is a significant difference for this question. This provides evidence that the visual aids and animations provided in the PowerPoint presentation were efficient in combating common misconceptions previously mentioned. Question 12, Burning a candle is an endothermic reaction since heat is absorbed to

initiate the reaction, also showed high significance which is a common misconceptions adopted by many students. The visual aids/ animations provided in slides in Appendices A.2.15-A.2.16 and A.2.18-A.2.19, walked the student through the process step by step to better understand that more energy is given off when a candle is burning indicating the release of more energy which constitutes this reaction as an exothermic reaction, regardless of the source of energy being absorbed to initiate the reaction. Questions 9, 10, and 13 showed an increase in the results but not statistically significant. For Question 9 25% of students continued to believe that heat is always needed for a chemical reaction to occur. For Question 10 24% of students remain to believe that all chemical reactions converts matter to energy. Majority of students answered Question 13 correctly in the pre-surveys so significance was not shown since there wasn't much of a difference between pre- and post-survey data.

Results obtained from surveys taken by student participants 1 month after the conclusion of the module displayed no statistically significant differences for attitudinal items as well as content knowledge items. Overall, only one attitudinal item "Science is one of my favorite subjects" showed a statistically significant increase, $p < 0.05$, pertaining to students' interest in science (Figure 29). Gender-based analysis did not show any significant differences for female or male participants as shown in Figures 30 and 31, respectively.

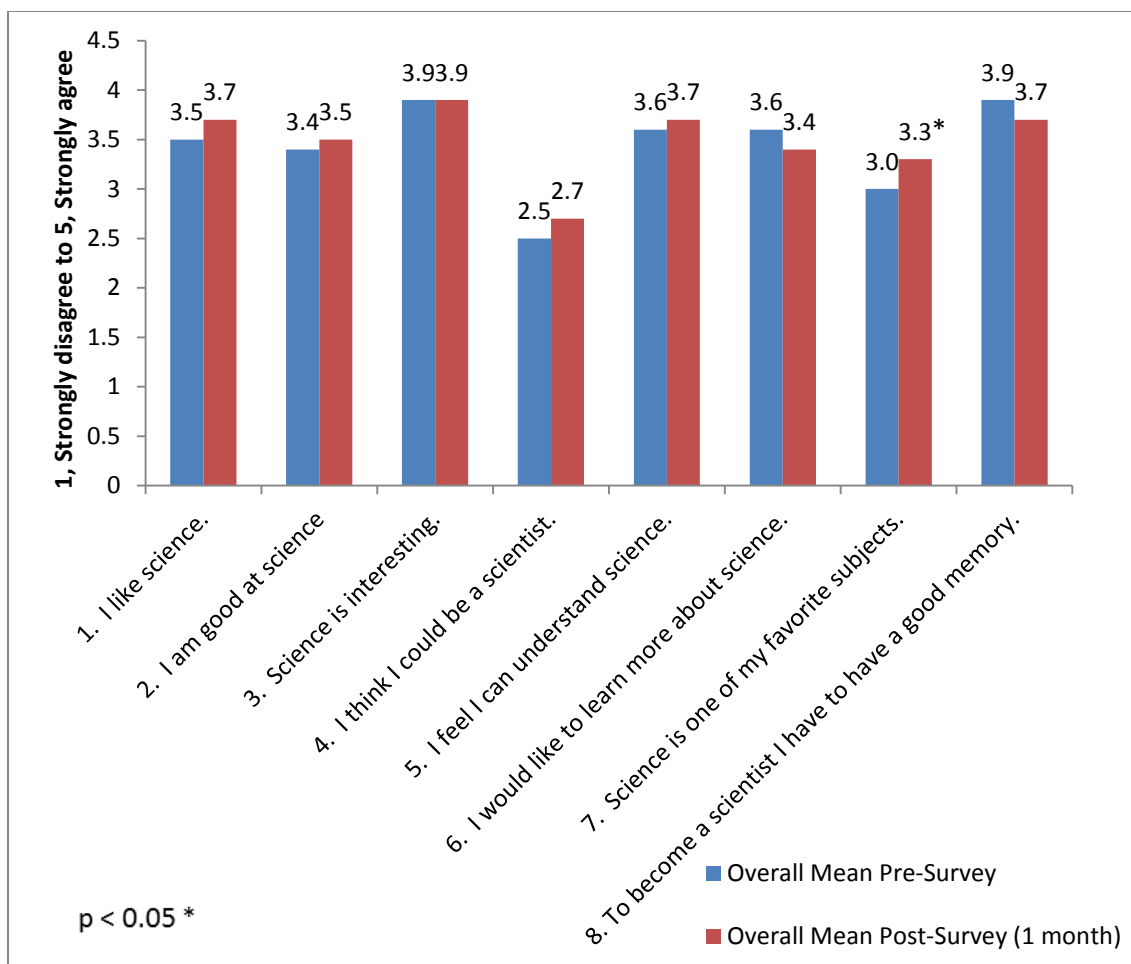


Figure 29. Overall attitudinal results 1 month after module presentation.

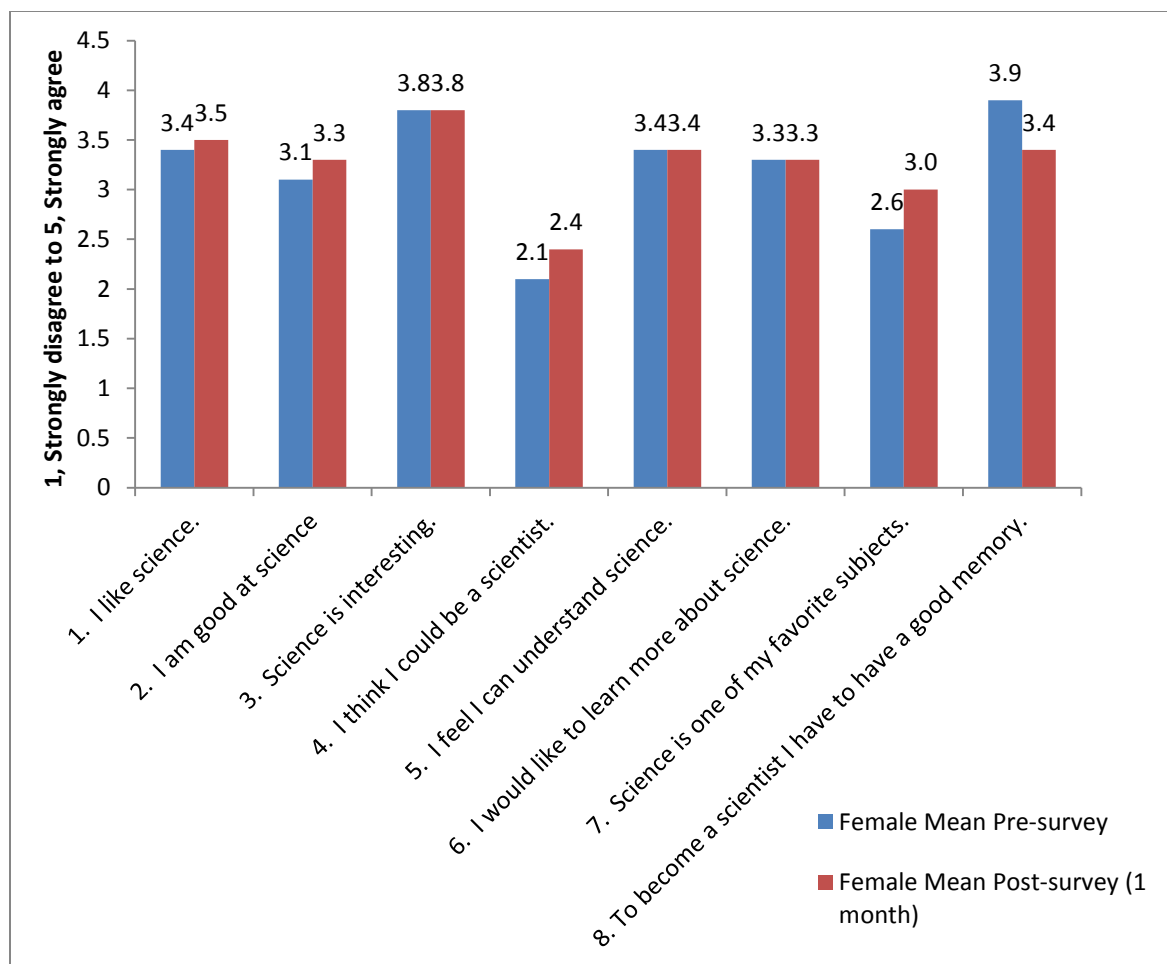


Figure 30. Female attitudinal results 1 month after module presentation.

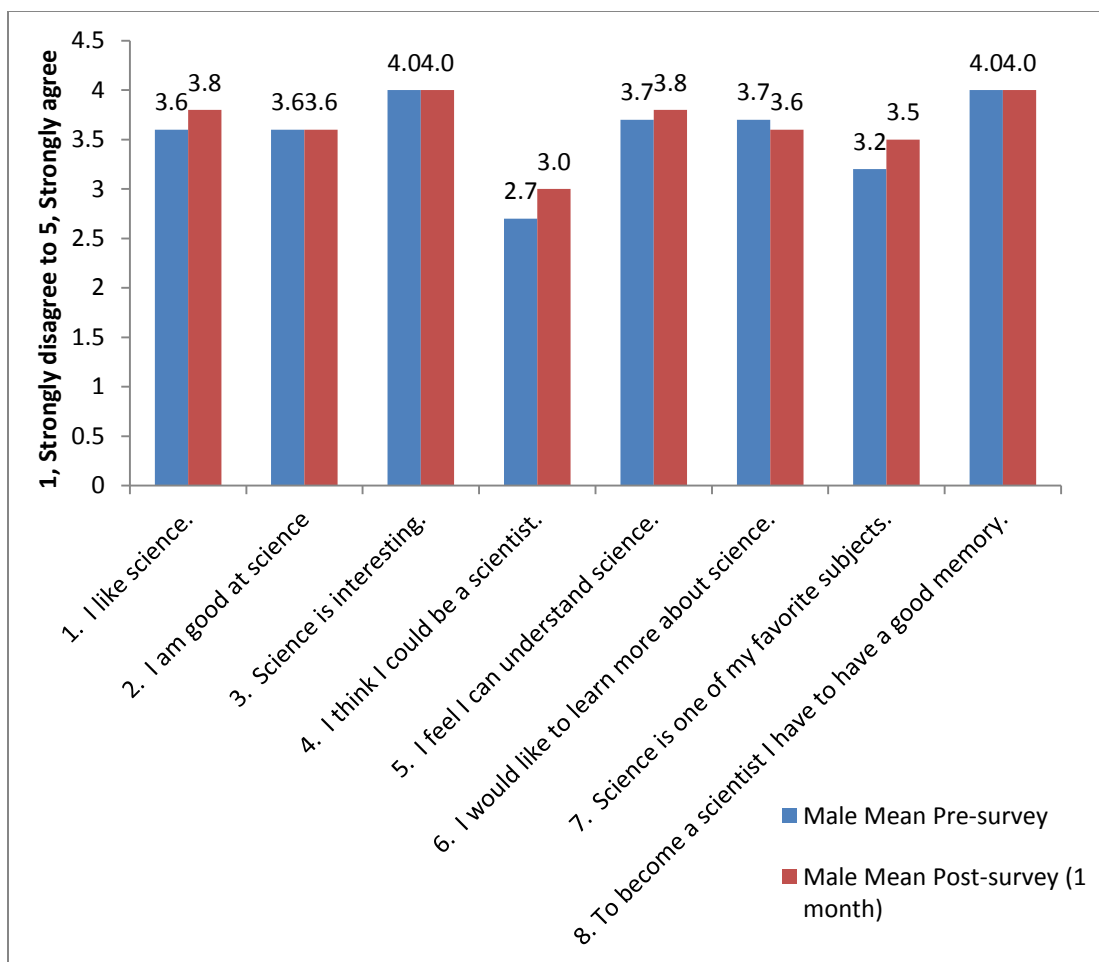


Figure 31. Male attitudinal results 1 month after module presentation.

Analysis of content knowledge items from surveys taken one month after the conclusion of the module showed statistically significant increases ($p < 0.05$) for 1 out of 5 items which included Question 11, “Which of the following could represent a chemical reaction?” (Figure 32). Gender-based results for content knowledge questions from surveys taken 1 month after the conclusion of the module mirrored the results of the data that was observed immediately after the conclusion of the module. There was a significant difference for Question 11 for male participants and Question 12 for female participants (Figures 33 and 34).

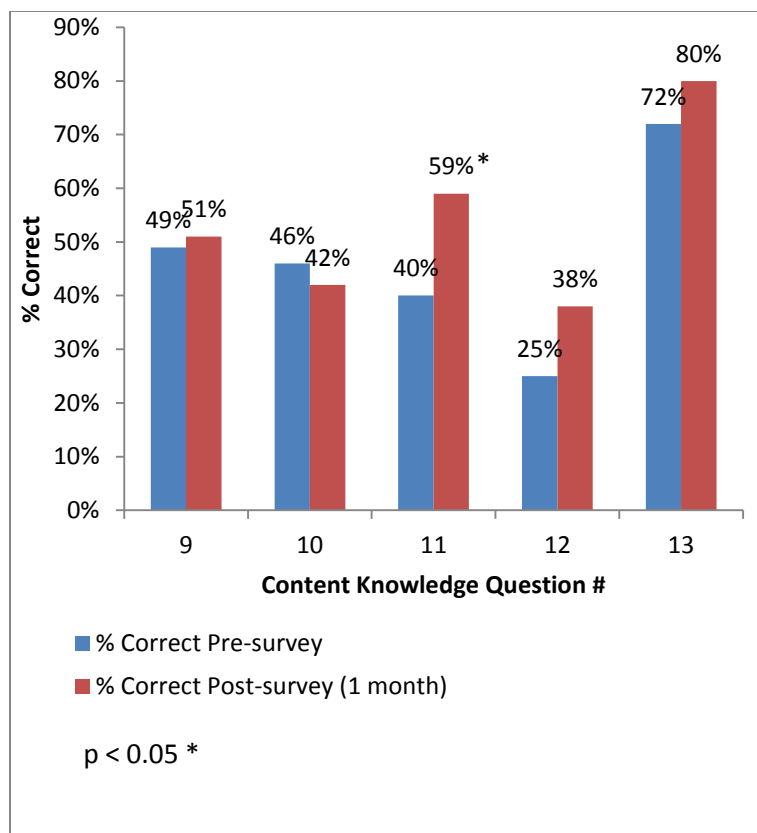


Figure 32. Overall content knowledge results 1 month after module presentation.

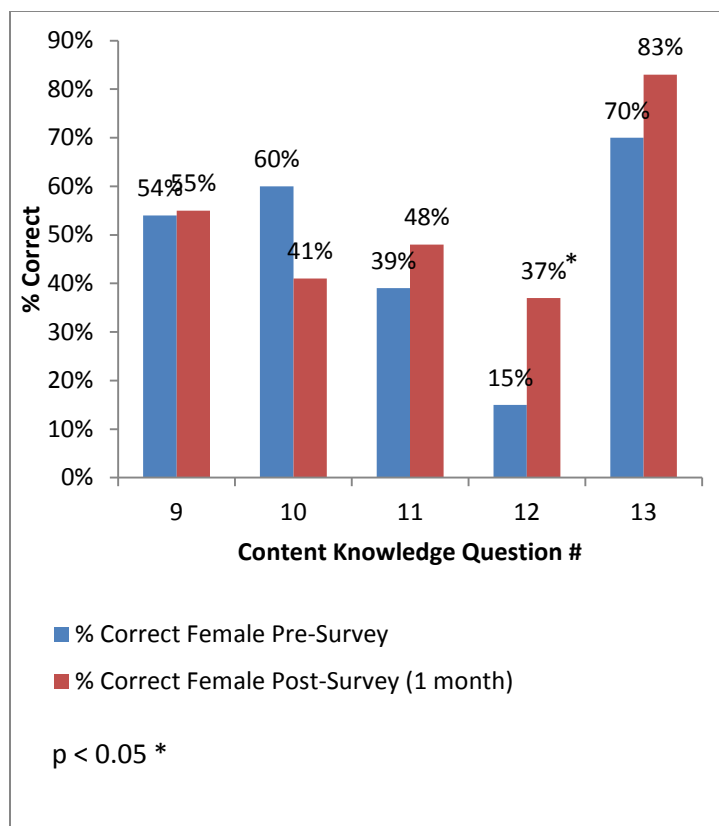


Figure 33. Female content knowledge results 1 month after module presentation.

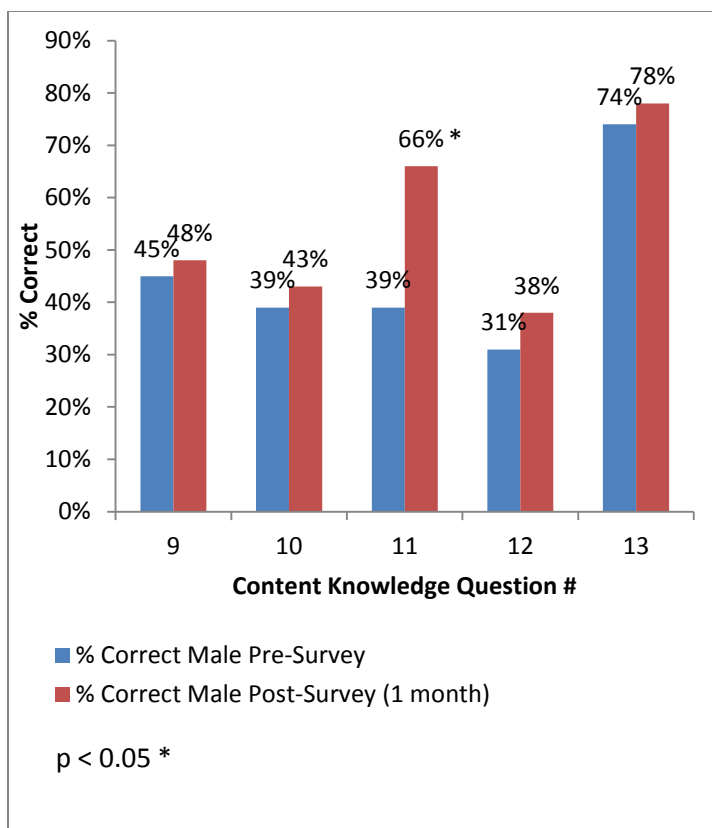


Figure 34. Male content knowledge results 1 month after module presentation.

The primary objective of this project was to develop a module that would efficiently improve students' attitude and self-confidence in science as well as address common misconceptions involved in energy changes in chemical reactions. Overall, the results indicated that because of the use engaging visual aids and demonstrations and the opportunity for students to be able to participate in hands-on experiments there was an observed increase in students' interest in science and self-confidence as well as an improvement in content knowledge. Immediately following the module attitudinal results was efficacious in increasing students' interest by showing a significant increase in "I like science," Science is one of my favorite subjects," and "I would like to learn more about science." Students' science self-efficacy results, also immediately following the completion of the module, displayed a measurable increase in "I

am good at science,” and “I think I can be a scientist.” Contrastingly, post-surveys taken one month after the conclusion of the module resulted in a decline of data significance with only one attitudinal significant increase in “Science is one of my favorite subjects.” This outcome comes as no surprise since immediately following the conclusion of the module the students’ vividly remember how much they enjoyed the use of hands-on experiments and visual aids that were presented to them and found the instructional method intriguing. It is possible that the decline in students’ interest and self-efficacy between the post-survey taken immediately after compared to the 1-month after post-survey may have been due to the limited one-day experience. After the completion of the module teacher’s carried on with their traditional instructional method that provided a lack of demonstrations and hands-on experiences. There was a significant gain in knowledge that was observed for both post-surveys which efficiently measures the efficacy of the visual aids and hands-on experiments were in explaining the content. The students were able to retain the same information over a period of a month. Although, the results of this project provided positive feedback of the proposed new instructional methods there are some limitations to the collected data. Therefore, the issues can be addressed by a set of modifications. One approach could be to present the study to a more diverse group of students and a larger sample size to gain more variance in the sample. Another approach is to include a second day for instruction so that the experience may have a longer-lasting effect on the students. The last approach is to train teachers on how to incorporate hands-on activities and demonstrations in their instructional strategies, thereby improving teacher effectiveness in the classroom. Ultimately, this may have a more lasting effect on the students’ interest and engagement in science and in developing a larger population of students’ intent to persist in science.

2.4 Conclusions

Students' attitude towards science seemed to increase after the presentation of the teaching module and displayed significance for 5 out of 8 attitudinal questions. Students were able to identify the common misconceptions of chemistry reaction, energy, and matter. Pre- and post-presentation analysis of the common misconceptions displayed an increase in students' content of knowledge by showing that many students were able to identify the misconceptions and learn from their previous mistake. The content knowledge analysis displayed significance for 2 out of 5 content knowledge questions supporting the idea of providing students with hand-on experiments helps to better convey the taught material. Drawings of their perceptions of a scientist showed that each gender portrayed their own gender as the scientist showing that their depictions are not gender-based. Some drawings displayed the "Einstein syndrome" which shows that this image of a scientist still exists. In addition, surveys will need to be administered after several months to measure long-term retention.

2.5 References

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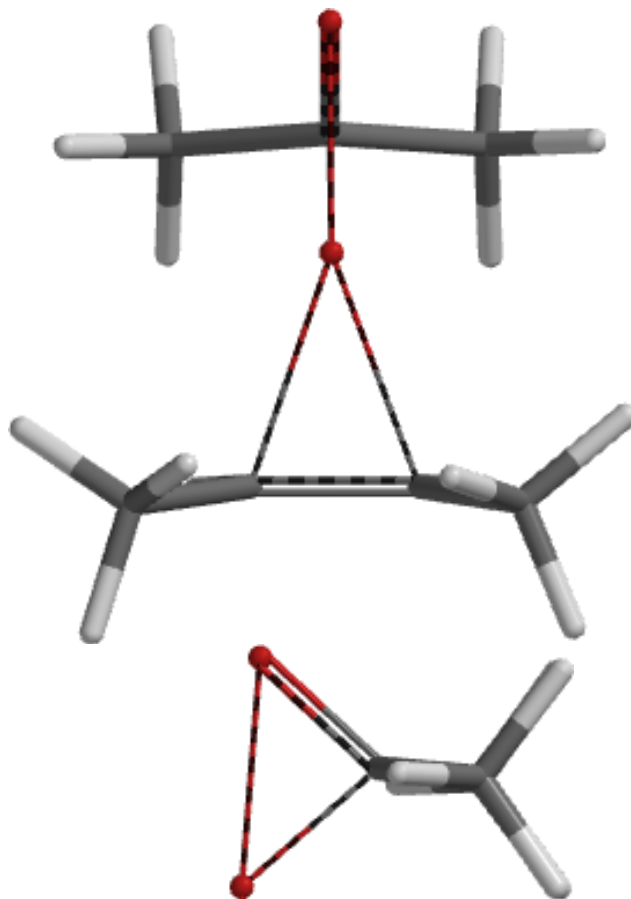
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APPENDICES

Appendix A.1.1 Transition state geometry epoxidation of *cis*-2-butene by dimethyldioxirane.

Front view :

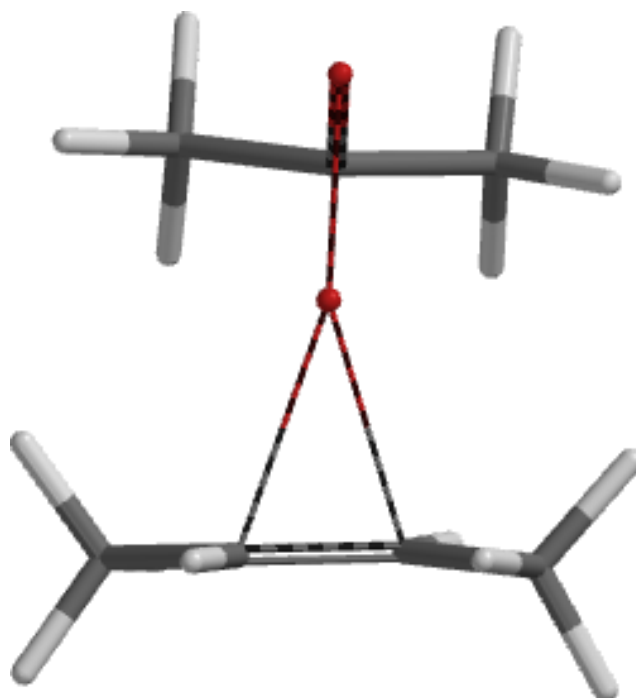


Side view :

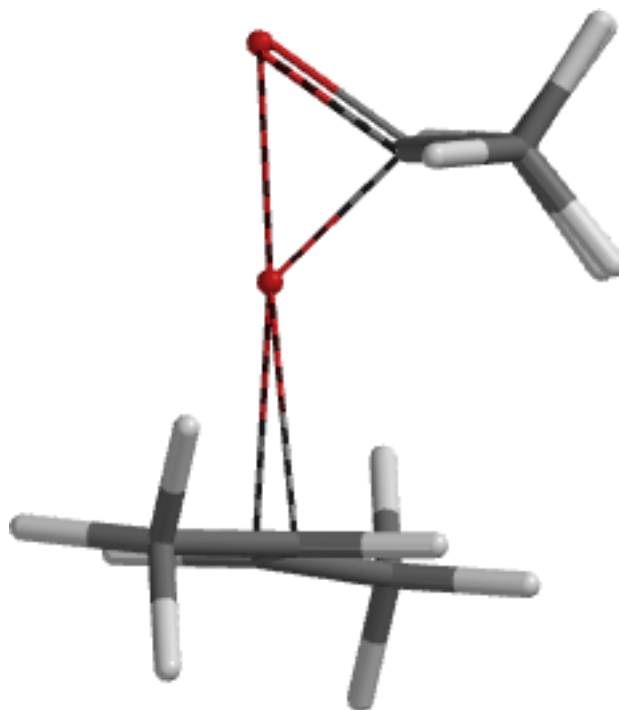


Appendix A.1.2 Transition state geometry epoxidation of *trans*-2-butene by dimethyldioxirane.

Front view :



Side view :

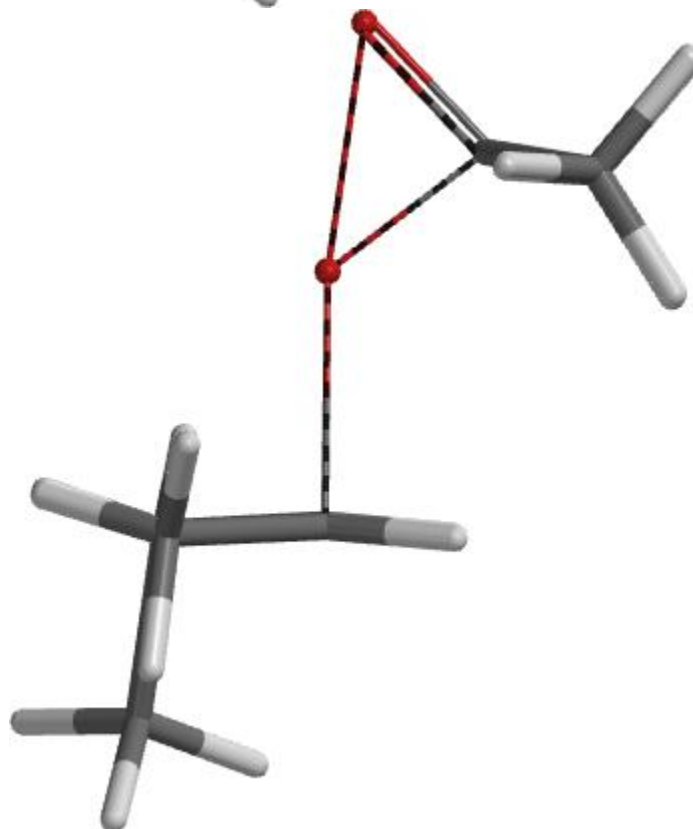


Appendix A.1.3 Transition state geometry epoxidation of *cis*-2-pentene by dimethyldioxirane.

Front view :



Side view :

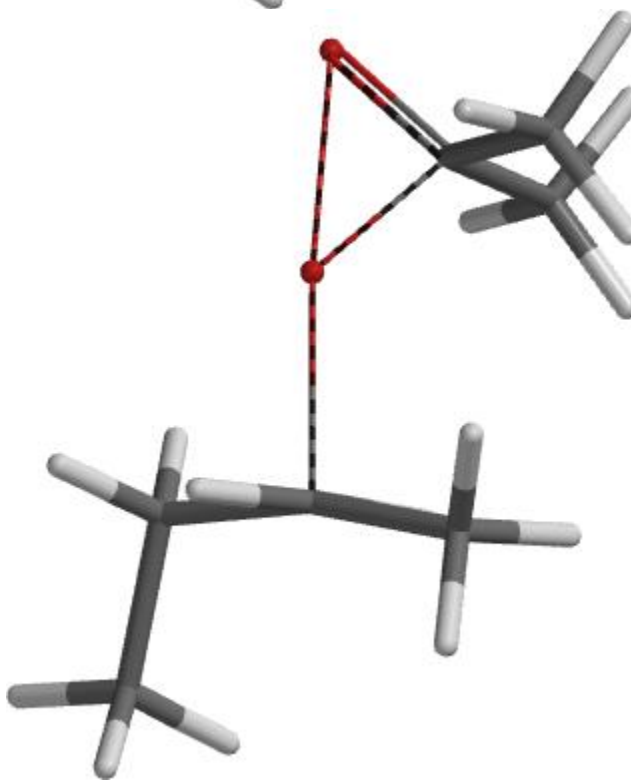


Appendix A.1.4 Transition state geometry epoxidation of *trans*-2-pentene by dimethyldioxirane.

Front view :

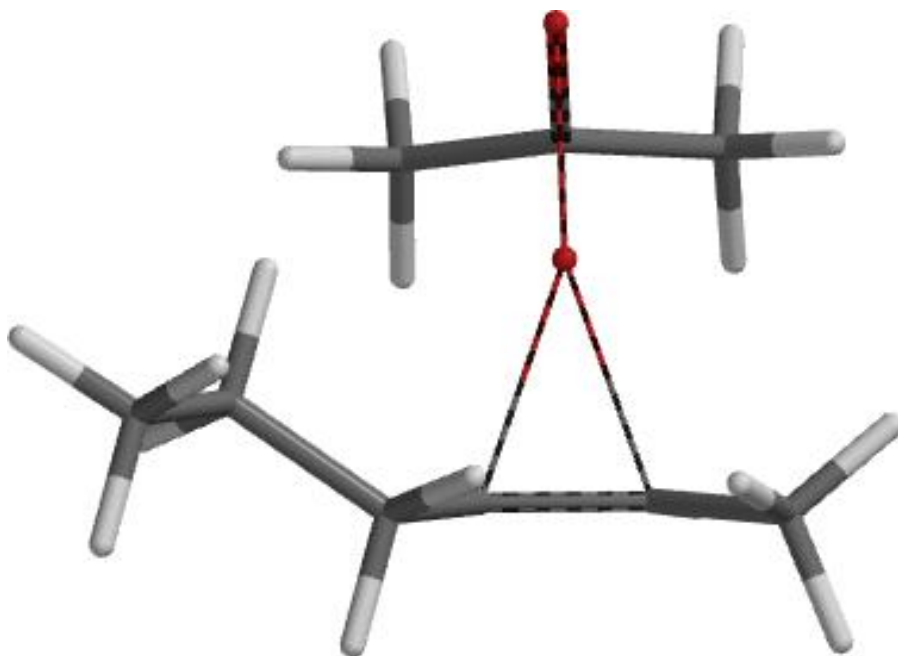


Side view :

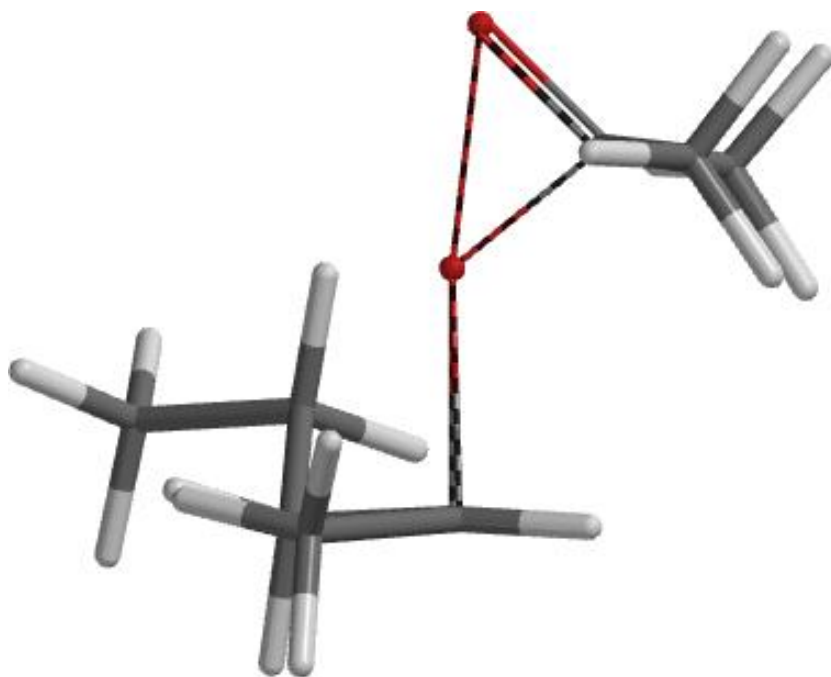


Appendix A.1.5 Transition state geometry epoxidation of *cis*-2-hexene by dimethyldioxirane.

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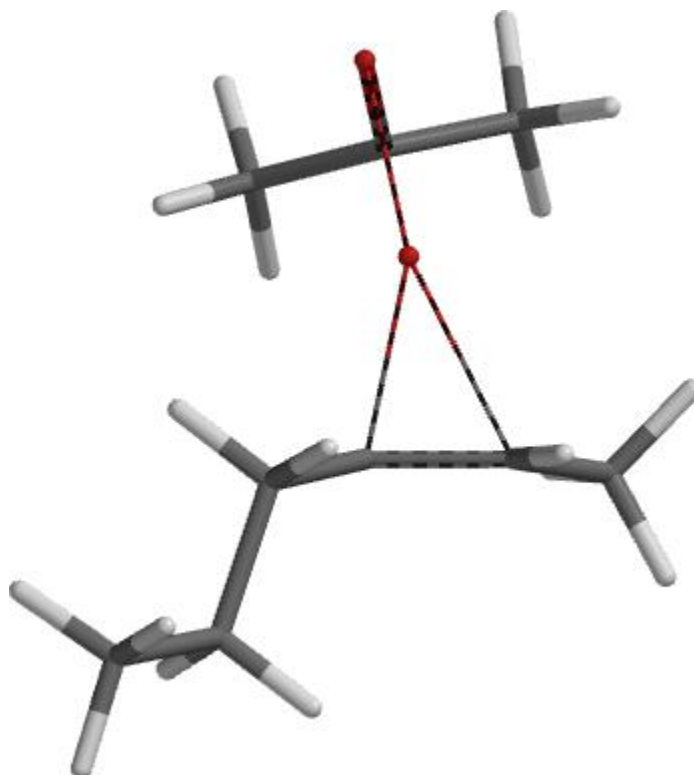


Side view :

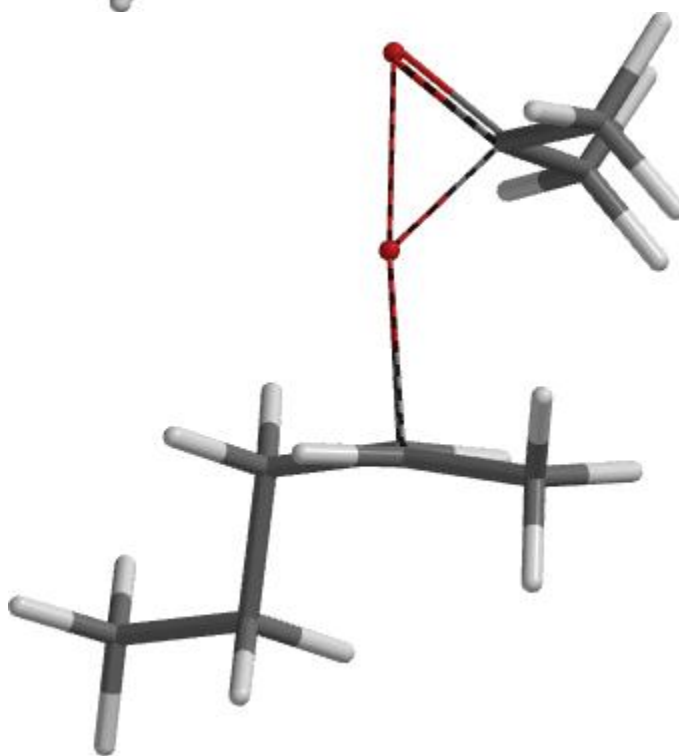


Appendix A.1.6 Transition state geometry epoxidation of *trans*-2-hexene by dimethyldioxirane.

Front view :

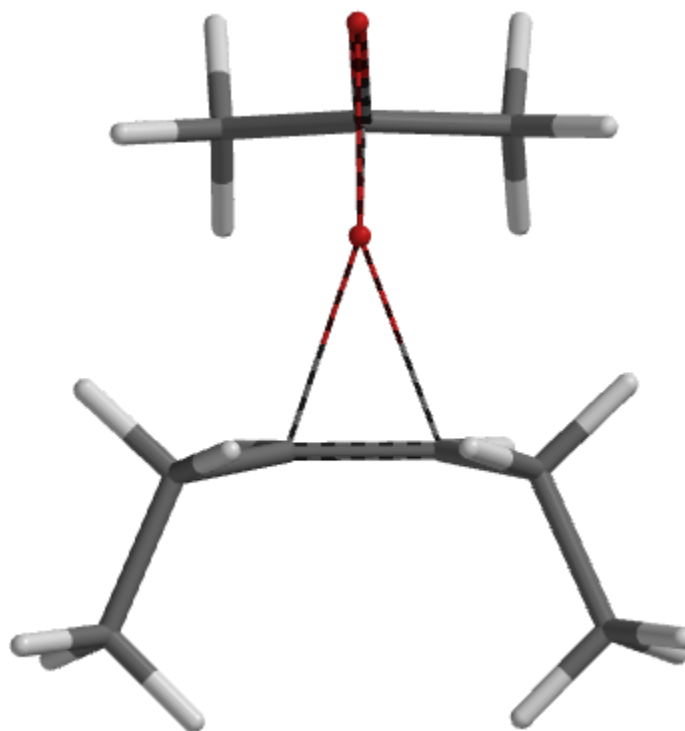


Side view :

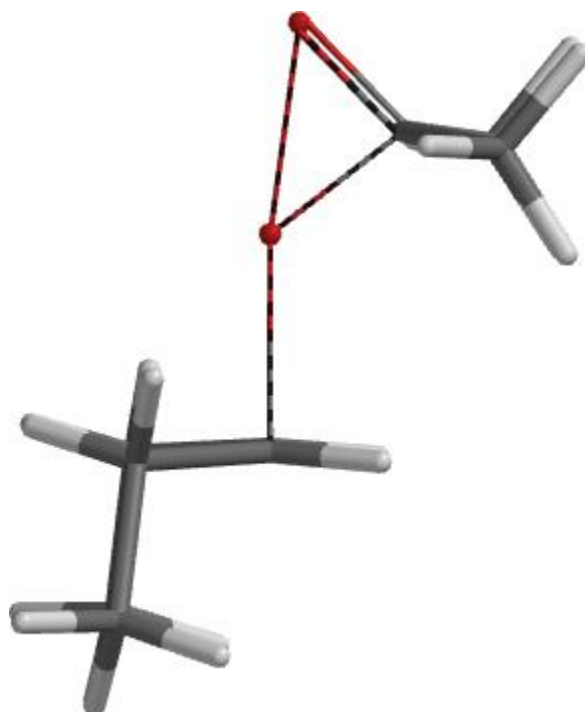


Appendix A.1.7 Transition state geometry epoxidation of *cis*-3-hexene by dimethyldioxirane.

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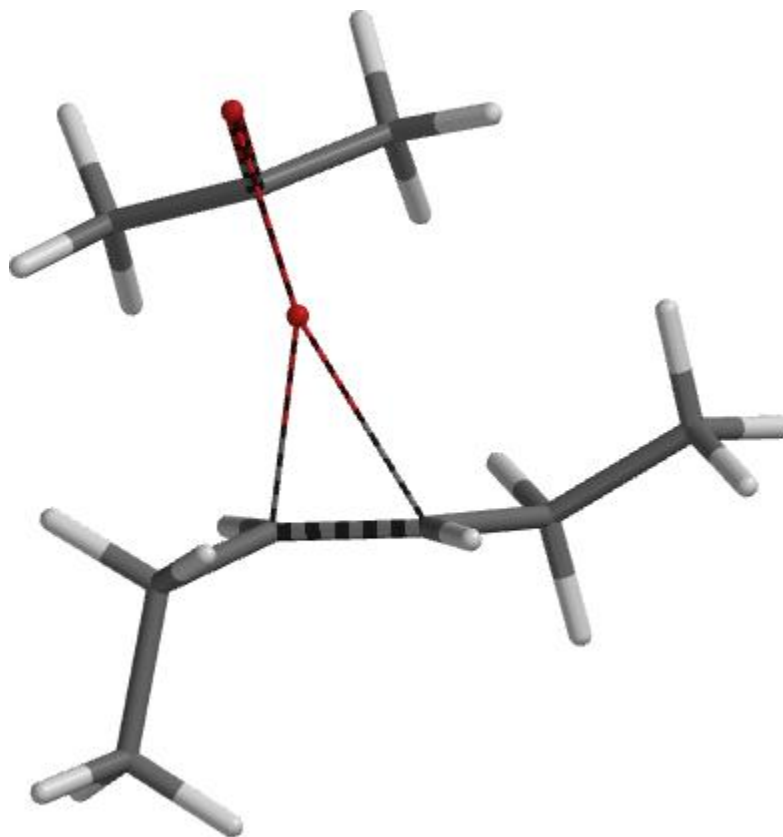


Side view :

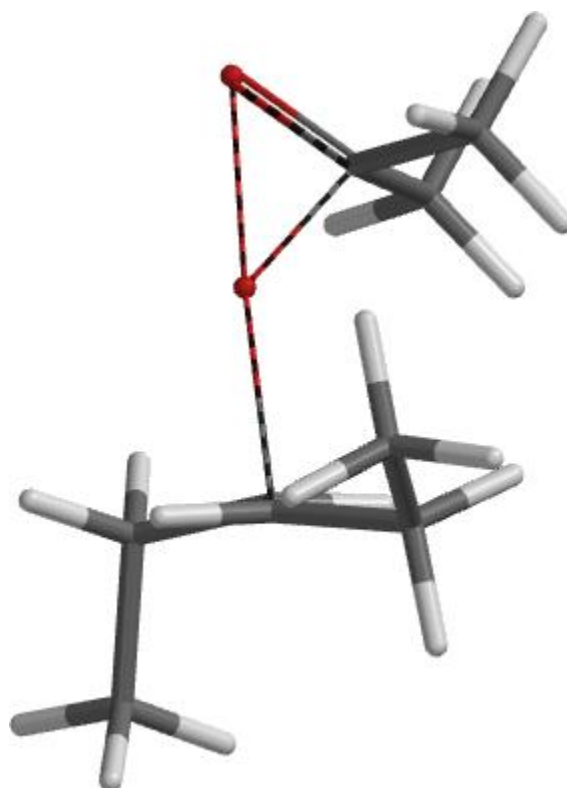


Appendix A.1.8 Transition state geometry epoxidation of *trans*-3-hexene by dimethyldioxirane.

Front view :

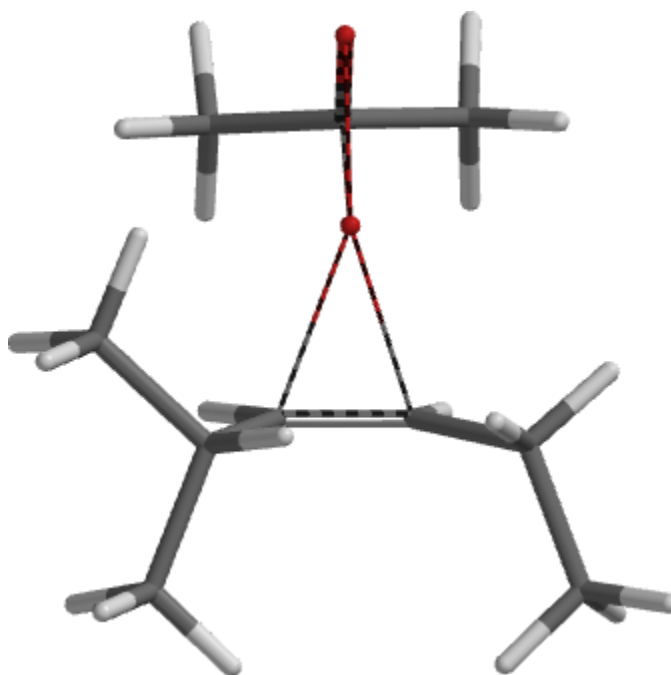


Side view :

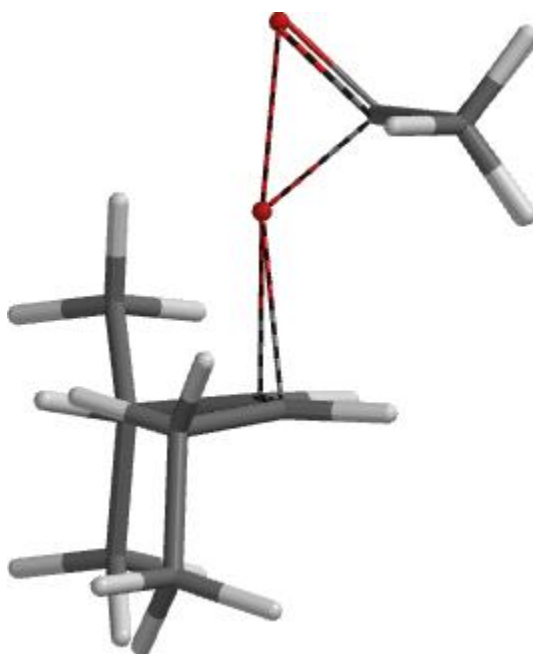


Appendix A.1.9 Transition state geometry epoxidation of *cis*-2-methyl-3-hexene by dimethyldioxirane.

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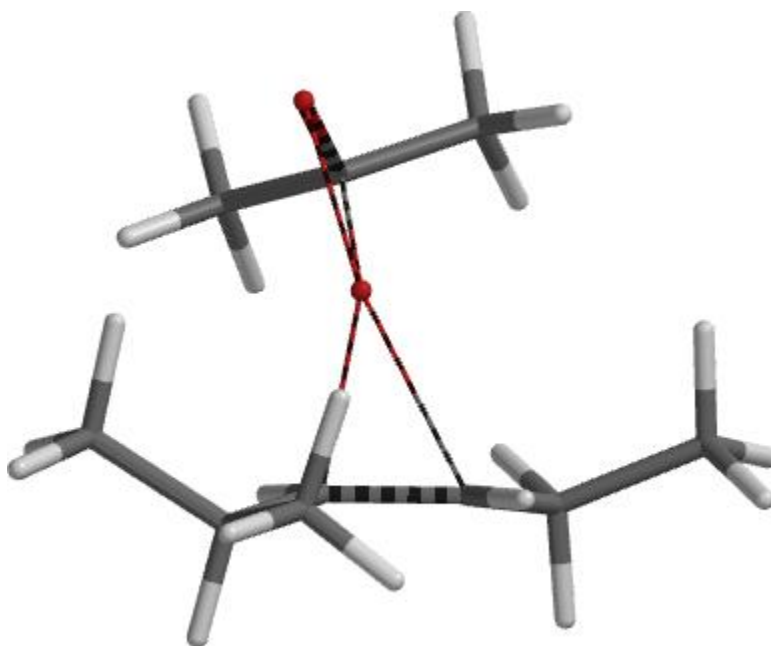


Side view :

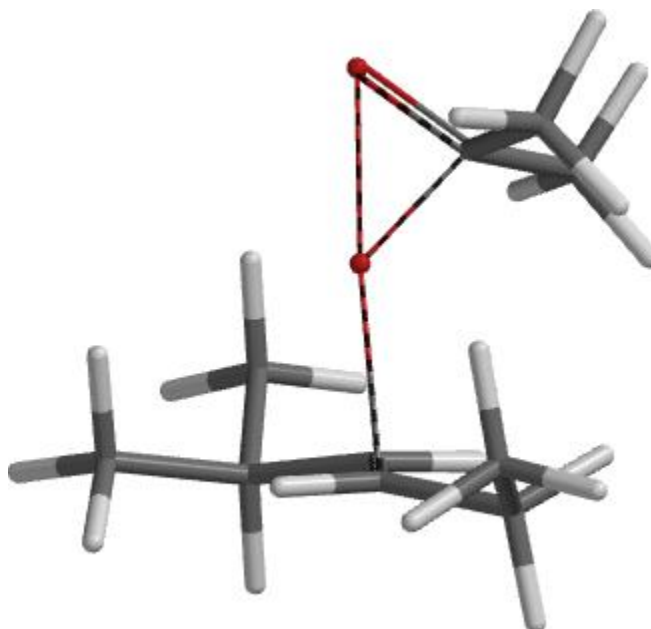


Appendix A.1.10 Transition state geometry epoxidation of *trans*-2-methyl-3-hexene by dimethyldioxirane.

Front view :

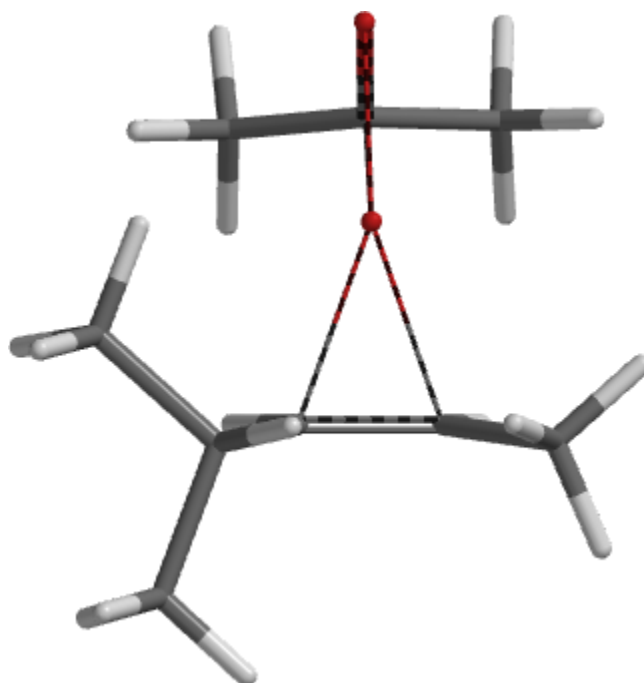


Side view :

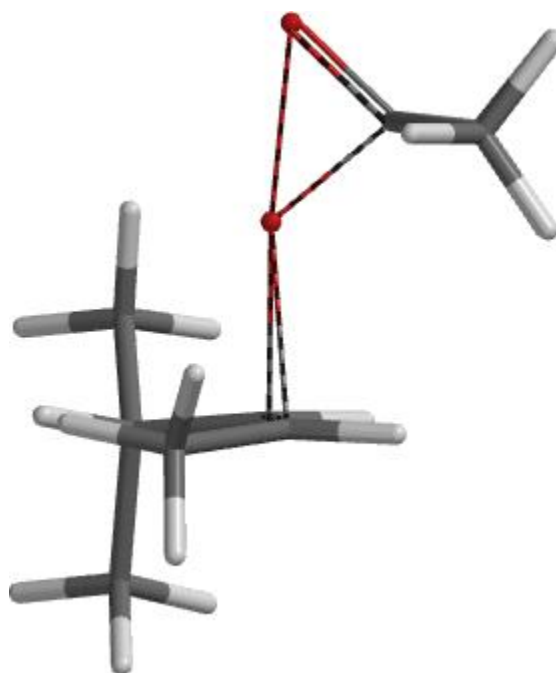


Appendix A.1.11 Transition state geometry epoxidation of *cis*-4-methyl-2-pentene by dimethyldioxirane.

Front view :

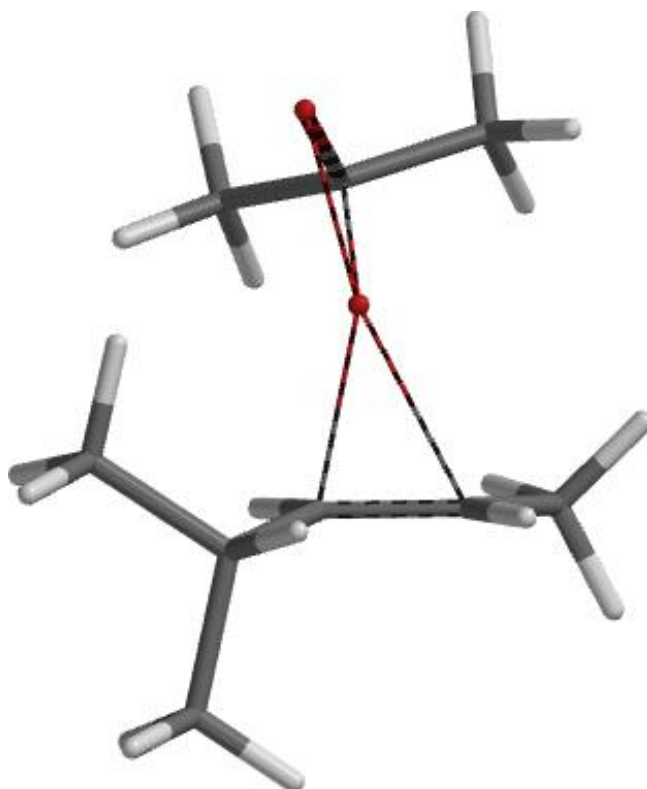


Side view :

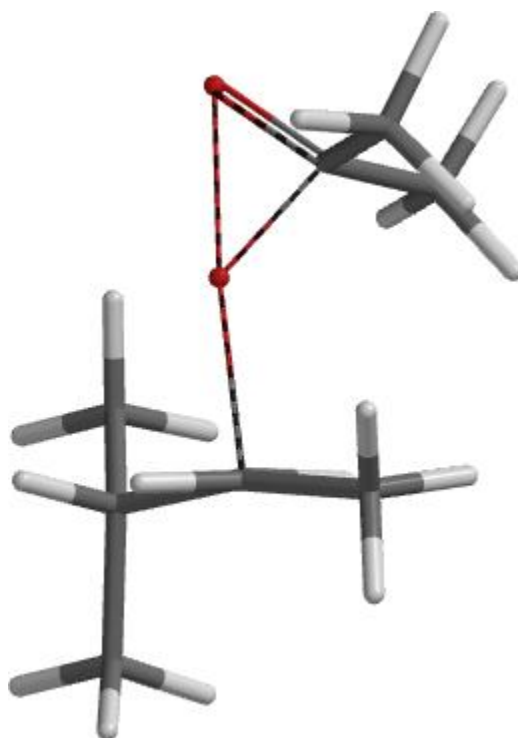


Appendix A.1.12 Transition state geometry epoxidation of *trans*-4-methyl-2-pentene by dimethyldioxirane.

Front view :

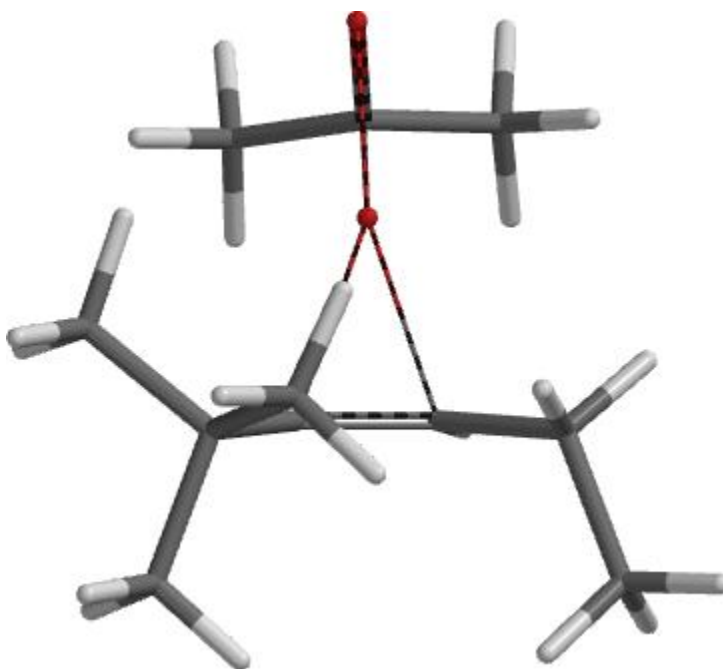


Side view :

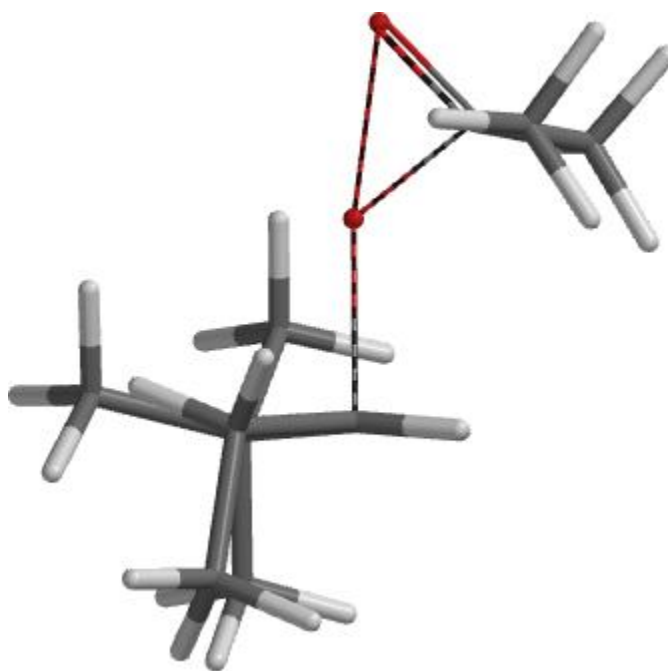


Appendix A.1.13 Transition state geometry epoxidation of *cis*-2,2-dimethyl-3-hexene by dimethyldioxirane.

Front view :

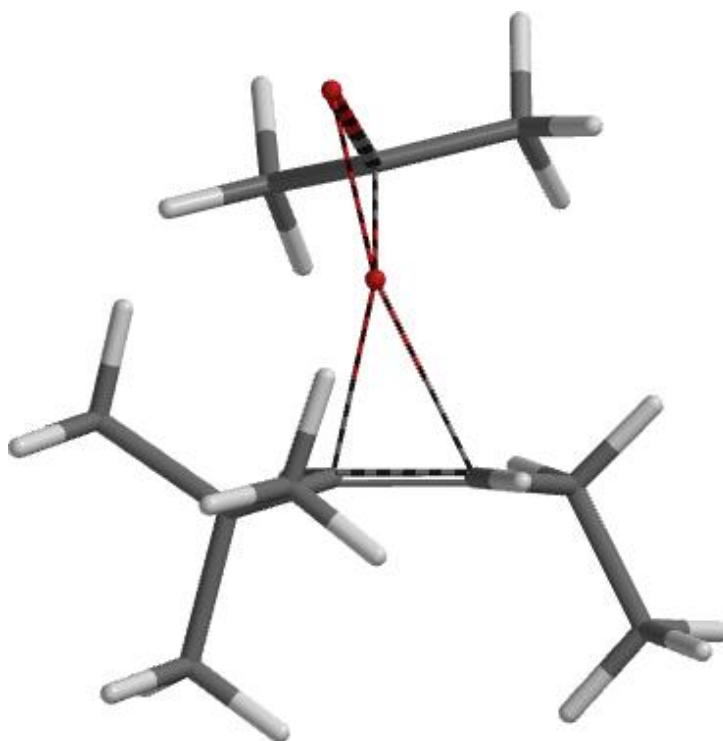


Side view :

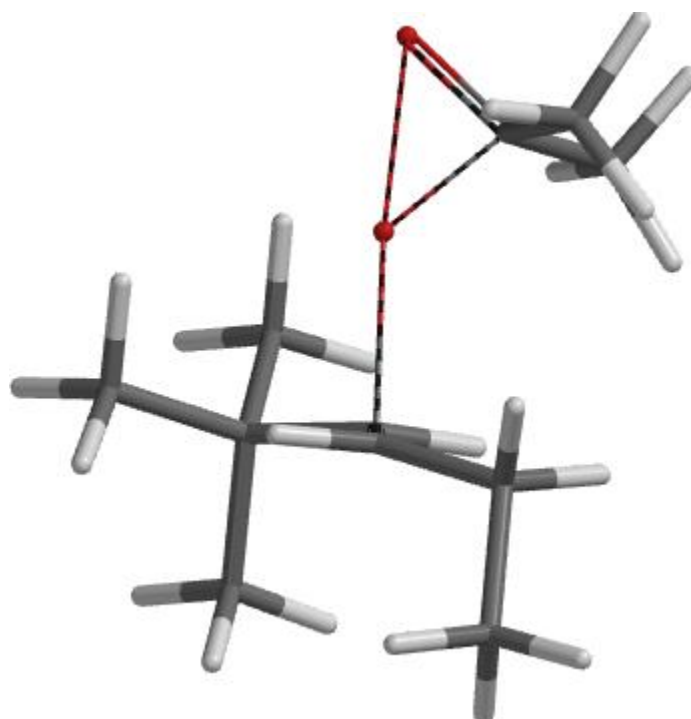


Appendix A.1.14 Transition state geometry epoxidation of *trans*-2,2-dimethyl-3-hexene by dimethyldioxirane.

Front view :

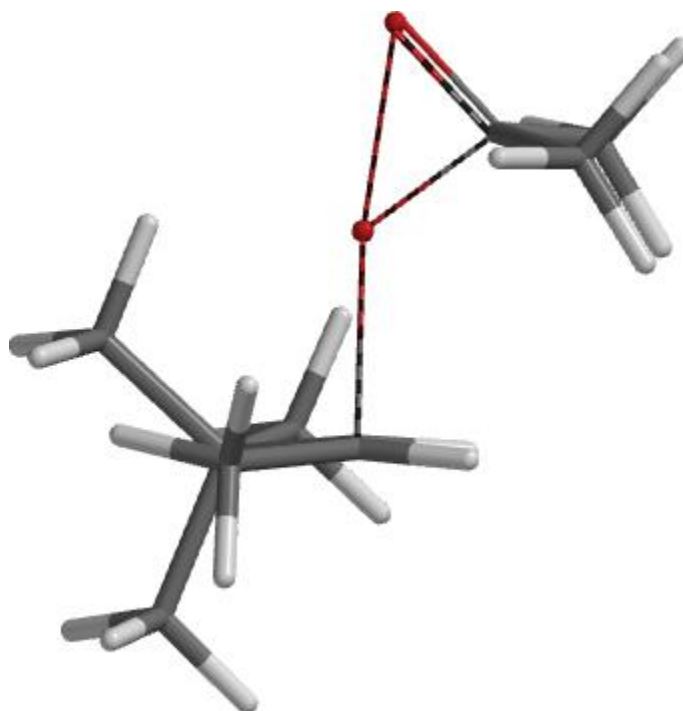


Side view :

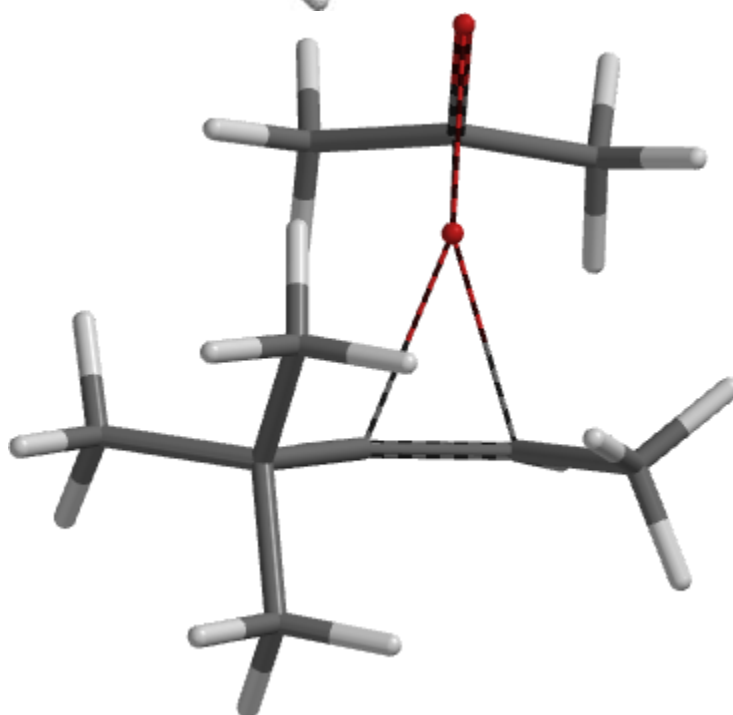


Appendix A.1.15 Transition state geometry epoxidation of *cis*-4,4-dimethyl-2-pentene by dimethyldioxirane.

Front view :

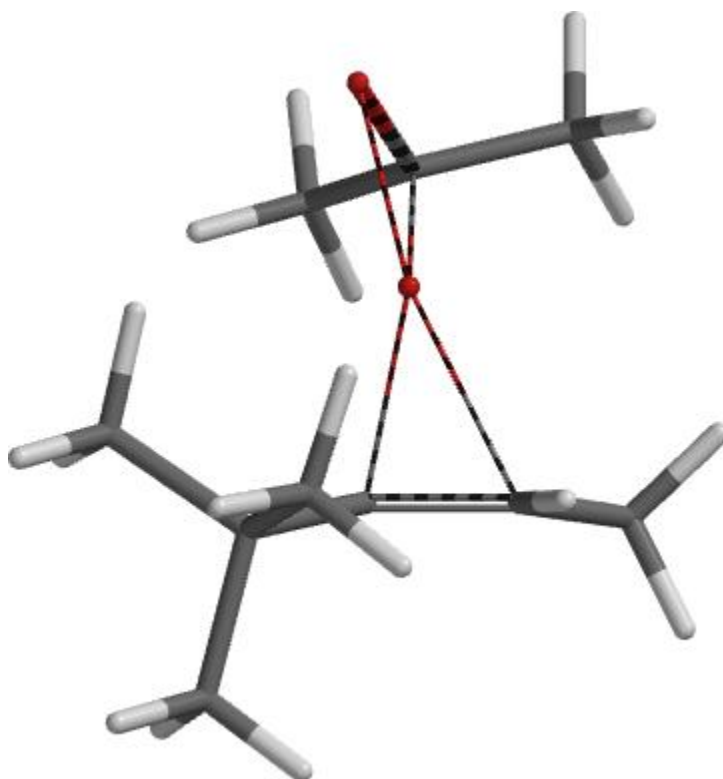


Side view :

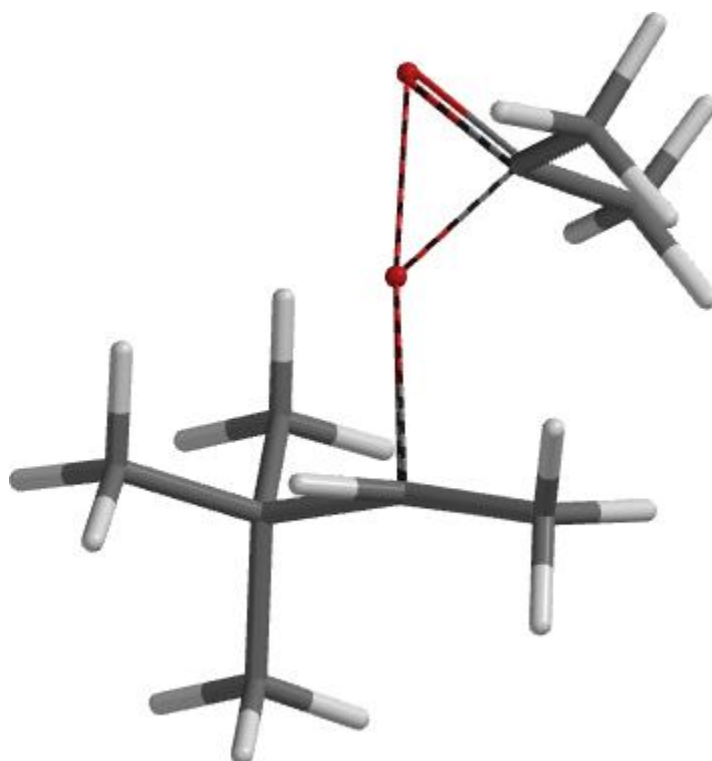


Appendix A.1.16 Transition state geometry epoxidation of *trans*-4,4-dimethyl-2-pentene by dimethyldioxirane.

Front view :



Side view :



Appendix A.2.1 Physical and chemical changes worksheet for student's observations (blank copy).



Hot or Cold, Does it Matter?

School Name:

Grade:

Date:

PHYSICAL AND CHEMICAL CHANGES

Ivory Soap Experiment

Instructions:

1. Place the Ivory soap on the microwavable plate.
2. Put the soap in the microwave for 1 minute.
3. Remove the soap from the microwave and let it cool.
4. Record your observations. What do you see?
5. Try to wash your hand with the soap and the water that is provided in the cup.
6. Record your observations

Observations:

Penny Experiment

Instructions:

1. Using the tweezers place your dull penny halfway in the vinegar/salt solution.
2. Leave the penny halfway in the solution for 30 seconds.
3. Remove the penny from the solution. What do you see?
4. Record your observations.

Observations:

Appendix A.2.2 Endothermic/Exothermic worksheet for student's observations (blank copy).



Hot or Cold, Does it Matter?

School Name:

Grade:

Date:

ENDOTHERMIC/EXOTHERMIC PROCESSES: Where does the HEAT go?

Citric Acid and Sodium Bicarbonate Experiment

Instructions:

5. Record initial temperature of citric acid solution.
6. Carefully pour the sodium bicarbonate (blue labeled vial) into the citric acid solution and stir.
7. Record the initial and final temperatures according to the time checkpoints in the table below.

Initial Temperature: _____

Time checkpoints	Temperature	Δ Temperature
5 seconds		
15 seconds		
25 seconds		

$\Delta T = \text{Initial temperature} - \text{Final temperature}$

Observations:

Hydrogen Peroxide and Yeast Experiment

Instructions:

1. Record initial temperature of hydrogen peroxide solution.
2. Carefully pour the yeast (red labeled vial) into the hydrogen peroxide solution and stir.
3. Record the initial and final temperatures according to the time checkpoints in the table below.

Initial Temperature: _____

Time checkpoints	Temperature	Δ Temperature
5 seconds		
15 seconds		
25 seconds		

$\Delta T = \text{Initial temperature} - \text{Final temperature}$

Observations:

Appendix A.2.3 Pre-/post-survey for student's observations (blank copy).



Hot or Cold, Does it Matter?

Student Survey

School Name:		Date:				
Please circle the letter that tells whether you agree or disagree with the statements below.		Strongly Agree	Agree	In Between	Disagree	Strongly Disagree
1. I like science.		a	b	c	d	e
2. I am good at science		a	b	c	d	e
3. Science is interesting.		a	b	c	d	e
4. I think I could be a scientist.		a	b	c	d	e
5. I feel I can understand science.		a	b	c	d	e
6. I would like to learn more about science.		a	b	c	d	e
7. Science is one of my favorite subjects.		a	b	c	d	e
8. To become a scientist I have to have a good memory.		a	b	c	d	e

9. What is ALWAYS needed for a chemical reaction to occur? a. Heat to start the reaction. b. Enough energy to make the reaction occur. c. Stirring or shaking action to make the reaction occur. d. Reactants that have the same state of matter.	11. Which of the following could represent a chemical reaction? Atoms are represented by circles and molecules are represented by circles that are connected to one another. The different colored circles represent different types of atoms. a. <div style="text-align: center;"> </div>	12. Burning a candle is an endothermic reaction since heat is absorbed to initiate the reaction. a. True b. False
	b. <div style="text-align: center;"> </div>	13. Energy is released to the environment which reflects why exothermic reactions feel warm. a. True b. False
10. Which of the following statement is true about the role of energy in all chemical reactions? a. All chemical reactions use energy to create matter. b. All chemical reaction convert matter into energy. c. All chemical reactions either release or absorb energy. d. All chemical reactions create or destroy energy.	c. <div style="text-align: center;"> </div>	Just for fun, draw your version of a chemist!

Ethnicity/Race: Black _____ White _____ Hispanic _____ Asian _____ Native American _____ Pacific Islander _____ Other _____	Gender: Male _____ Female _____	Grade: _____
--	---------------------------------------	-----------------

Appendix A.2.4 Slide 1 for educational module.



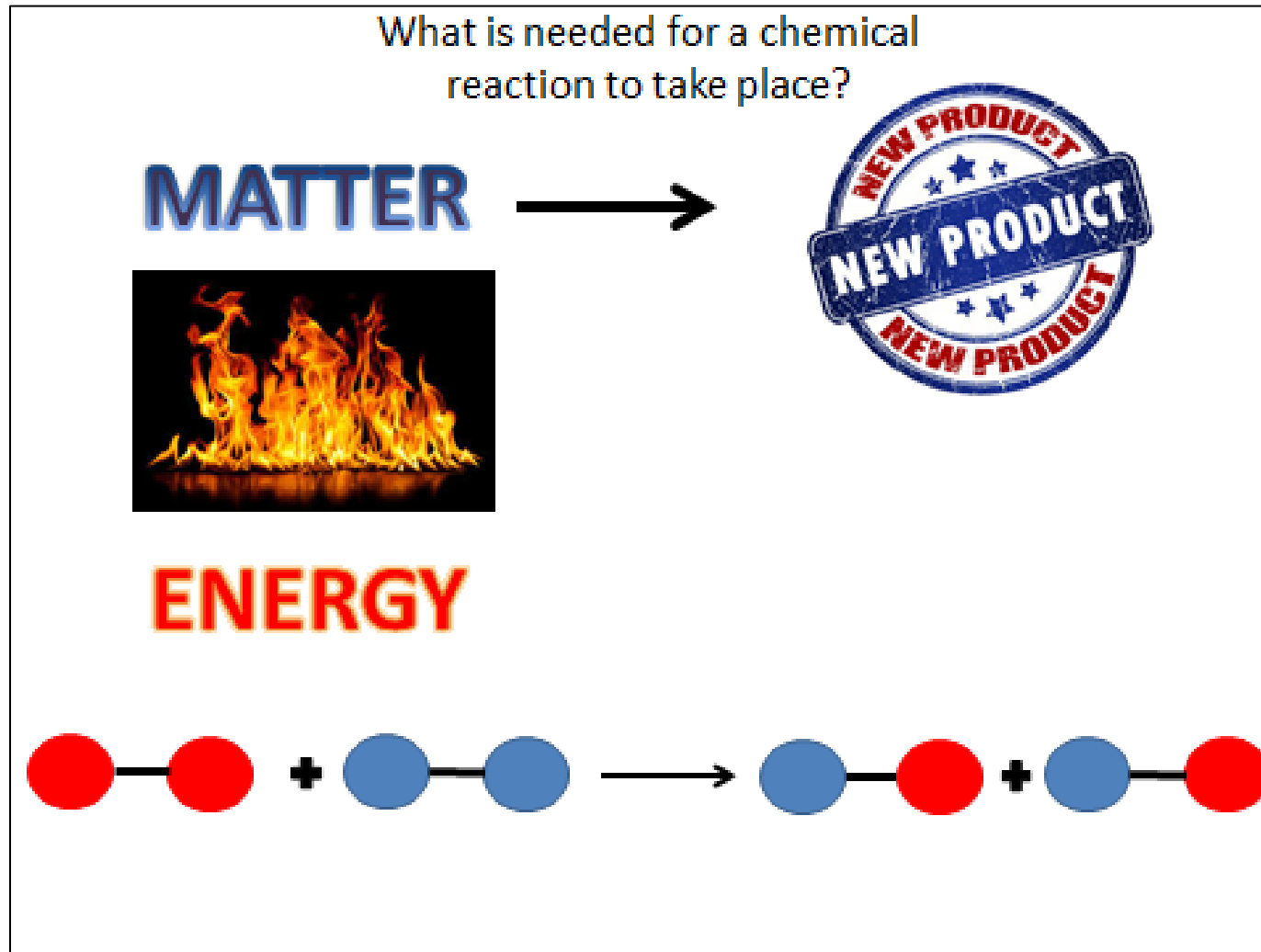
HOT or COLD: Does it matter?

Energy changes in chemical reactions

By: Davita McTush-Camp



Appendix A.2.6 Slide 3 for educational module.



Appendix A.2.7 Slide 4 for educational module.

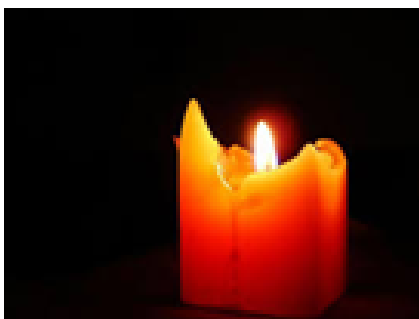
Do you have what it takes ??? Is this a chemical reaction???



Appendix A.2.8 Slide 5 for educational module.

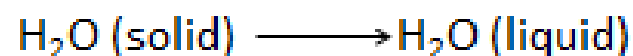
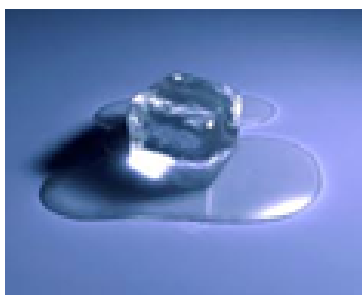
Matter can participate in **chemical** and **physical** changes.

Chemical change takes place at the molecular level and produces a new substance.



Paraffin (wax)

Physical change is a change in state or phase.



Appendix A.2.9 Slide 6 for educational module.



Let's Experiment!!!!



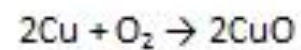
Appendix A.2.10 Slide 7 for educational module.

What happened???

Ivory soap experiment



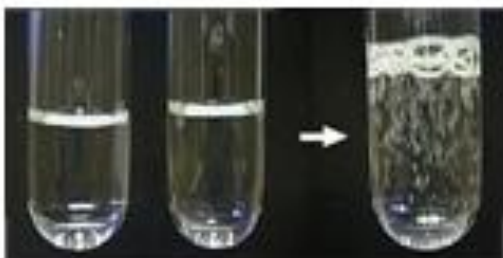
Penny experiment



Appendix A.2.11 Slide 8 for educational module.

How may we see that a chemical reaction
has taken place???

Formation of gas



Heat, light, odor emit



Color change



Solid formation



Appendix A.2.12 Slide 9 for educational module.

What controls the speed of a chemical reaction?

Temperature



Catalysts



Concentration of reactants



Appendix A.2.13 Slide 10 for educational module.

Thermal energy in chemical reactions

Thermal energy can be absorbed to start a chemical reaction and thermal energy can be released as a form of energy in a chemical reaction.

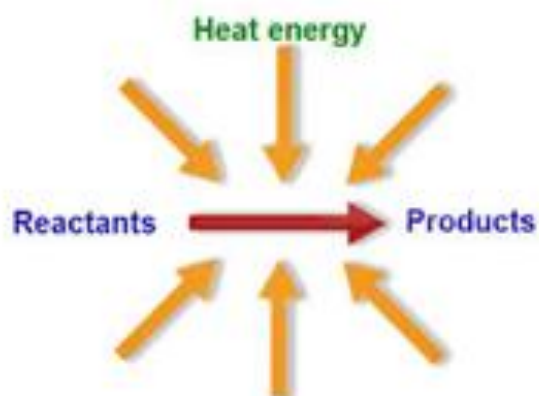
These types of chemical reactions can be described as **ENDOTHERMIC** and **EXOTHERMIC** reactions.



Appendix A.2.14 Slide 11 for educational module.

Endothermic reactions

Endothermic reactions- a chemical reaction that absorbs heat



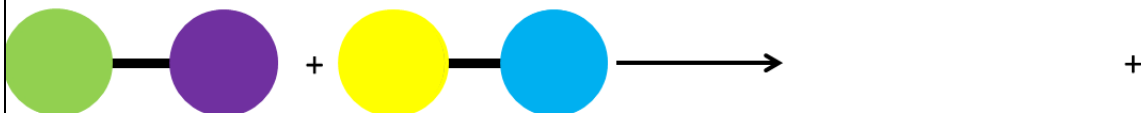
Think of it as heat Entering the chemical reaction for an Endothermic reaction.



Appendix A.2.15 Slide 12 (before animation) for educational module.

Endothermic reactions

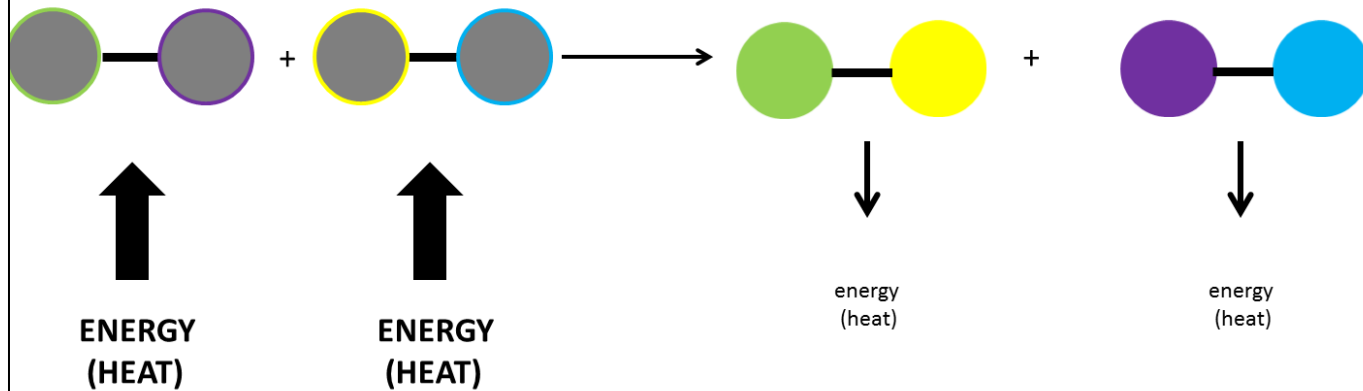
- Energy is absorbed to break the bonds of the reactants.
- Energy is released when the bonds of the products are formed.
- Since more energy is absorbed when the bonds are broken than is released when new bonds are formed, the reaction is endothermic and the temperature goes down.



Appendix A.2.16 Slide 12 (after animation) for educational module.

Endothermic reactions

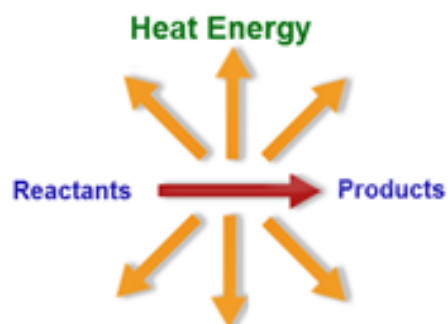
- Energy is absorbed to break the bonds of the reactants.
- Energy is released when the bonds of the products are formed.
- Since more energy is absorbed when the bonds are broken than is released when new bonds are formed, the reaction is endothermic and the temperature goes down.



Appendix A.2.17 Slide 13 for educational module.

Exothermic reactions

Exothermic reactions- a chemical reaction that releases heat



Ex: A burning candle

Think of it as heat Exiting the chemical reaction for an Exothermic reaction.

Appendix A.2.18 Slide 14 (before animation) for educational module.

Exothermic reaction

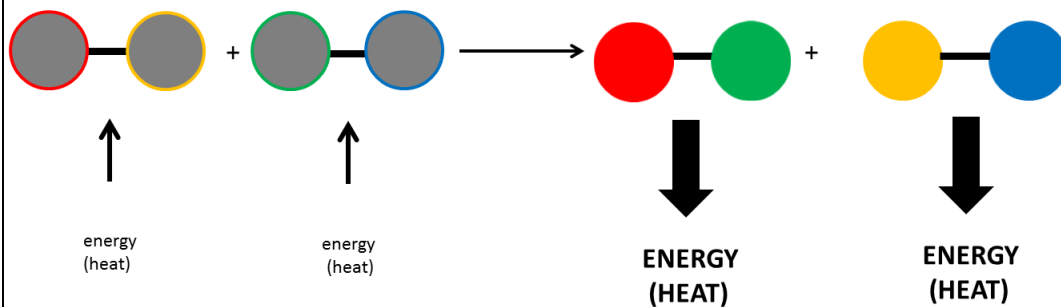
- Energy is absorbed to break the bonds of the reactants.
- Energy is released when the bonds of the products are formed.
- Since more energy is released when the bonds are formed in the products than is absorbed to break the bonds in the reactants, the reaction is exothermic and the temperature goes up.



Appendix A.2.19 Slide 14 (after animation) for educational module.

Exothermic reaction

- Energy is absorbed to break the bonds of the reactants.
- Energy is released when the bonds of the products are formed.
- Since more energy is released when the bonds are formed in the products than is absorbed to break the bonds in the reactants, the reaction is exothermic and the temperature goes up.



Appendix A.2.20 Slide 15 for educational module.

Light energy in chemical reactions: Chemiluminescence

Chemiluminescence is an exothermic chemical reaction that gives off light instead of heat as a form of energy.

Fireflies



Sea jelly



Crime scene



Glow sticks

Appendix A.2.21 Slide 16 for educational module.

Summary

- Chemistry is the study of matter, its structure and properties and the changes it undergoes.
- Chemical change takes place at the molecular level and produces a new substance. Physical change is a change in state or phase.
- Exothermic reaction is a chemical reaction that releases heat.
- Endothermic reaction is a chemical reaction that absorbs heat.
- Chemiluminescence is an exothermic chemical reaction that releases light as a form of energy.